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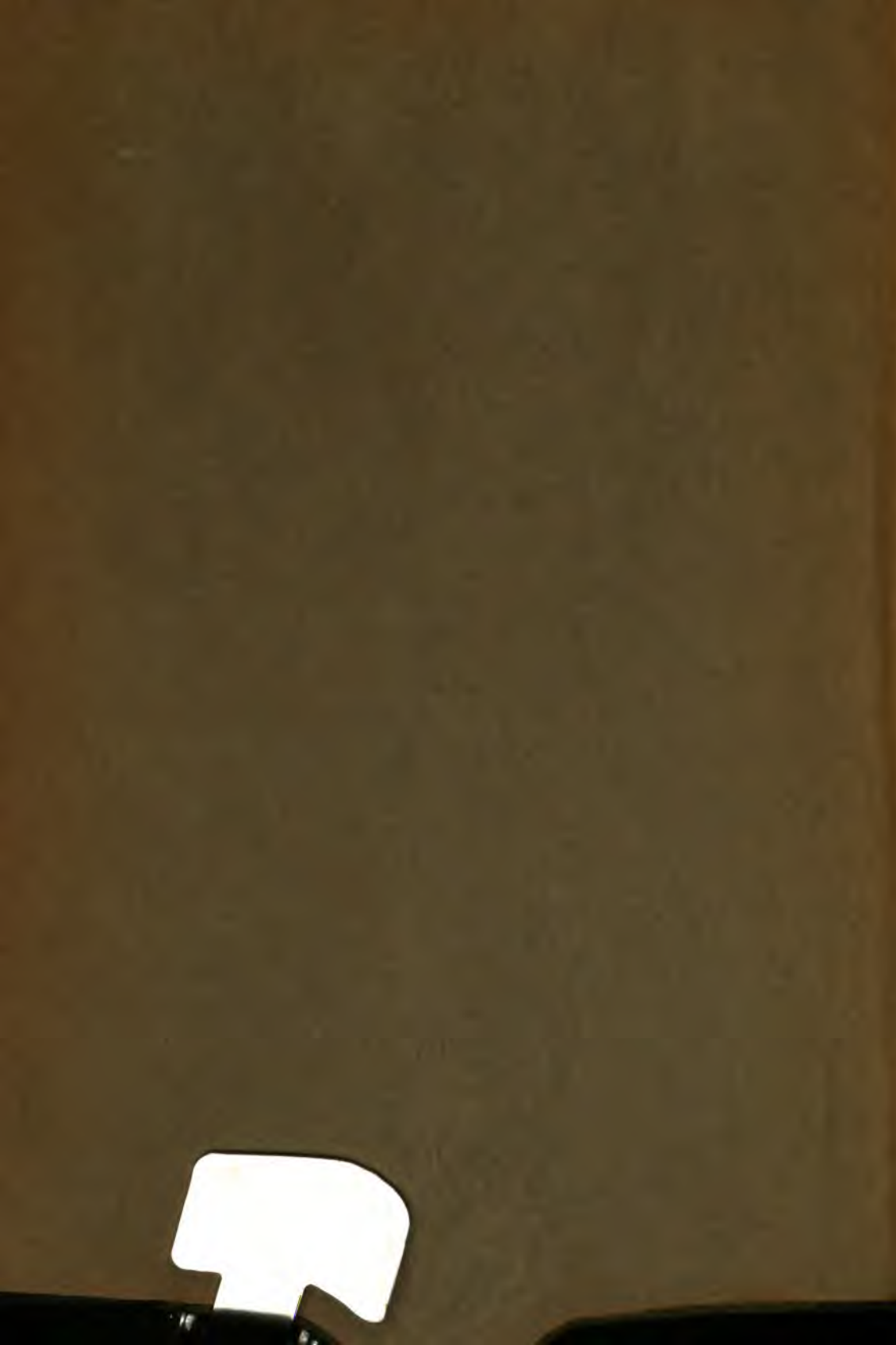
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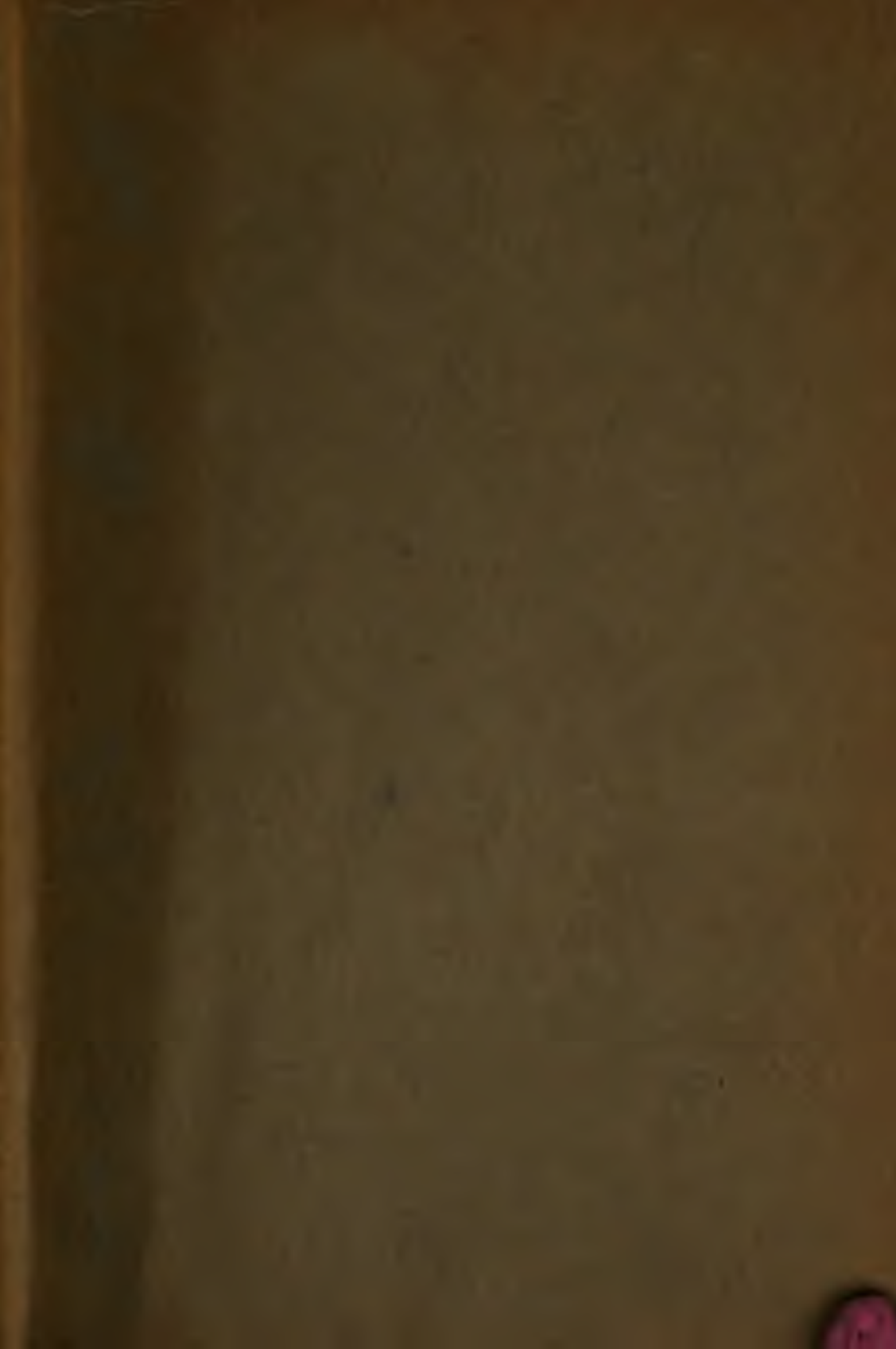
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Frontispice.

Pitch Lake—View E. of N. from point near center of E. side and within 200' of shore.

SOLID BITUMENS

THEIR

Physical and Chemical Properties

AND

Chemical Analysis

TOGETHER WITH

A Treatise on the Chemical Technology

OF

Bituminous Pavements

BY

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PREFACE.

This book has been written at the request of several friends. I began experimenting on bitumens while a student in Brown University in 1859. Interrupted by the Civil War, I again took up the work on the Pacific Coast in 1865 and it has been prosecuted almost continually until the present time, a period of forty years. Happy in the personal friendship of C. M. Warren, in whose laboratory I spent several months, I have used nearly every method of investigation that has been proposed in the United States and Europe, and have read nearly everything that has been published relating to bitumens from Boussingault's Memoir to the present time. It would be strange, if, with such experience, I had not learned much that might be useful to my fellow men. This is my apology for offering a work on solid Bitumens.

The word Asphalt has become so hackneyed through misuse, that I have avoided its use wherever possible.

While the work represents much of personal experience, my aim has been to offer everything of value relating to the subject, giving full justice to all, whether they agree with me or not. If anything essential has been omitted, it is done through inadvertence, without intention. So far as has been possible, reference has been made to original memoirs. I am aware that there may be instances in which I have not met the originals, in which case the wrong reference is accidental.

With these few words of explanation and apology, I dedicate my work to my fellow laborers in a field of vast extent and intricate paths, the boundaries of which no man living will discover.

S. F. P. .

New York, October 1, 1909.

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PART I.
THE NATURAL HISTORY OF
BITUMENS.

INTRODUCTION.

The exact meaning of the word "bitumen" has in recent years become involved in some obscurity. In antiquity, and, indeed, until a recent date, it had a definite meaning. For instance, in Genesis xi, 3, a Hebrew word occurs which designates the cementing substance used in constructing the walls of the tower of Babel. In the Septuagint this word is translated asphaltos, and in the Vulgate bitumen. In the Bishops' Bible of 1568, and in subsequent translations into English; the word is rendered "slime." In the Douay translation of 1600 it is "bitume." In the Protestant French translation it is "bitume." In Luther's German Bible it is "thon," the German word for clay. In removing the magnificent alabaster slabs that were used to adorn the palaces of Ninevah and Babylon, it has been discovered that the material used to cement and hold the slabs in position, was mineral pitch, softened by heat.

The word "asphaltum" is said to be derived from α, primitive and σφαλlos, "I cause to slip." It therefore signifies a substance that prevents one from slipping, and it was applied to the solid forms of bitumen that soften in the sun. This substance was not rare in so-called Bible lands, embracing the valley of the Tigris and Euphrates, the tablelands of Mesopotamia and the valley of the Jordan. It was of frequent occurrence along the shores of the Dead Sea, and was gathered and sold in the caravan trade that passed through the land of Moab and Petrea into Egypt, where it was sold for the linings of silos and cisterns and for use in embalming the dead. Cisterns and silos are still intact that were built in Petrea and Egypt, and lined with asphaltum from two to three thousand years ago, yet the manner of their construction and the locality from which the bitumen was obtained, and even by whom they were built, is at present unknown.

During the Middle Ages, asphaltum and other forms of bitumen appear to have found but few uses, and they are sel-

dom mentioned. The words bitumen, asphaltum, petroleum and naphtha appear to have been used with different meanings, and also interchangeably or synonymously; yet the words were generally used to signify a thing that was located and defined by further description, so that the bitumen of the Dead Sea was recognized as asphaltum, or solid bitumen; that of Zante as petroleum, etc.

It is only within the nineteenth century that any serious confusion in nomenclature has appeared, and then the trouble has arisen almost wholly from commercial considerations. About the year 1830, the French schist oil began to assume importance. Later, the Scotch paraffine industry arose, and during the decade from 1850 to 1860 extended from Scotland to the United States, into which both the material used and the methods of manufacture were imported. In France the materials used were properly called "the bituminous shales of Autun." In Scotland the material was called "boghead coal," "boghead shale" and "boghead mineral;" it was also called torbanite. The expense attending the importation of the boghead shale into the United States, led the Downer Kerosene Oil Co., of Boston, Mass., and Portland, Me., to make an exclusive contract for the Albertite of New Brunswick. It was called Albert Coal, asphalt, pitch, etc.; and, for commercial reasons, became the subject of a very important lawsuit, in which, as experts, scientific men gave very conflicting testimony, one party claiming that the material was asphaltum, and the other that it was coal. It was finally decided that the material was not coal and did not belong to the crown.* This decision established the fact, both in law and science, that asphaltum is not coal.

In line with this decision, the late Dr. T. Sterry Hunt, as long ago as 1863,† separated pyrobituminous from bituminous minerals. The fundamental principle underlying the use of this word "pyrobituminous," exists in the fact, that schists, shales and all crude coals, except anthracite, together with many other substances, wholly or in part of organic origin,

*Taylor's "Statistics of Coal," Philadelphia, 1855, p. 516. Taylor's deposition before the Supreme Court at Halifax, N. S., respecting the asphaltum mine at Hillsborough, Philadelphia, 1851. On a New Variety of Asphalt, C. M. Wetherell. Trans. Am. Philos. Society (N. S.), 10, 353.

†Am. Jour. of Science (2) 35 p. 157. Chemical and Geological Essays. J. R. Osgood & Co., Boston, 1875.

yield products that resemble bitumens on being heated to destructive distillation. Why this clearly scientific, and very convenient distinction has not been made the foundation upon which all scientific definitions relating to bitumens proceed, is difficult to explain. Yet, until this distinction is fully recognized, writers will continue to mix up bituminous coals, schists of Autun and Mansfield, boghead mineral, etc., with all sorts of bitumens to the infinite confusion of the discussion of bitumens. These coals, schists and shales, while containing a large amount of organic matter, are nearly as insoluble in the solvents of bitumen, viz.: ethyl ether, chloroform, benzole, etc., as they are in distilled water; hence Dr. Hunt made the action of these solvents exclusive of the two classes of substances. All true bitumens are miscible with, or almost wholly soluble in chloroform, a test that clearly separates them from pyrobituminous minerals. So-called "asphaltic coals" are not coals at all, but are simply geologically old asphaltums.

The word bitumen therefore is a generic term that includes a large number of substances that are brought together by reason of possessing certain physical properties in common. Under this generic term the species are not yet clearly defined. The words, natural gas, naphtha, petroleum, maltha, asphaltum and asphalt, are not names of things having a constant and well recognized chemical composition. When a true system of nomenclature shall have been adopted, under which the species and subspecies under bitumen shall receive appropriate names, it will be found that a species may occur in nature in any or all of the several conditions, from natural gas to asphaltum. A true system, therefore, must name and classify the bitumens themselves.

In any attempt to define bitumen, it is at once apparent that there are a large number of minerals, consisting in part of bitumen that are, strictly speaking, rocks. To this class of substances belong the Seyssel limestone and sandstone of the upper valley of the Rhone, the Limmer and Ragusa rocks, the Niagara limestone of Chicago, the bituminous limestones and sandstones of Utah and Oklahoma, the Turrellite of Texas, the sandstones of Kentucky, the Athabasca

River and California. These occur in beds of sedimentary or crystalline rock, often of immense extent and thickness, impregnated with bitumen of varying consistency and quality. Sometimes, the bitumen is found to be quite fluid after it is separated from the rock, but it is never solid. In some instances it may become solid, by exposure to atmospheric influences, and in others not. Mr. Malo and other French writers have called these rocks "asphalte." They have also called asphaltum by the same name, as if the things were identical and the words synonymous. German authors have generally used the French word. Among English speaking peoples great confusion has followed an attempt to use the French word, as the most unlike things are called "asphalt." The author suggested using the word *asphalte* to designate only the different bituminous rocks, but in a late letter, Prof. George Lunge informs me that the French and German languages present difficulties, wellnigh insurmountable when such an attempt is made.

The so-called Trinidad pitch, as it is found in and around the lake, is a unique mixture of bitumen, with mineral and vegetable matter, which is inflated with gas. When removed from the deposit, the water rapidly dries out, the gas escapes, the mass becomes brittle and changes from a brown to a blue-black color, acquiring a sticky consistency as it loses water. If the dried mass is put into water, the water is reabsorbed and the mass again becomes brown. At a rough estimate, less than 25 per cent of the natural cheese pitch that fills the lake is bitumen. Trinidad pitch is only in part bitumen and is a complex mineral species, for which the author has elsewhere suggested the name "Parianite," from the formation in which the celebrated lake occurs.*

From the earliest mention of the substance in Greek and Roman literature, to within what is termed the modern period, the typical asphaltum of commerce has been the solid bitumen found on the shores of the Dead Sea. In later years, as the knowledge of mankind has extended, not only respecting the surface and extent of the surface of the earth, but also respecting the things found in and upon that surface, the word

*Journal of the Franklin Institute, Nov., 1895.

asphalt has been used to designate a number of substances that may be arranged in a series, the members of which differ but slightly in those closely related, but very widely in the extremes. The confusion arising from this cause has been of slow growth, and has led to inconvenience only within comparatively recent years.

In the English translation of Boerhaave's Chemistry published in London in 1732, which was a classic in its time, asphaltum, with other forms of bitumen, is classed as a variety of sulphur. At present these substances are no longer associated, but a great lack of clearness has arisen from the inability of many writers to appreciate the differences that exist between substances with which they are locally familiar, and other similar, but in many respects quite different materials found in other localities. There is, too, a disposition to name any solid mineral containing bitumen, asphaltum or asphalt, without regard to either the kind or amount of impurities with which the bitumen is associated. Another source of confusion is found in the fact that for various reasons those substances more or less closely allied to the natural solid bitumens that are by-products of many technical processes, have been named and described as asphaltum or asphalt. These substances are often not bitumen at all.

Still another source of confusion is the use of the word pitch as an equivalent for asphaltum. This word comes down through all modern languages from an unknown antiquity and has been used with its equivalent to designate the tarry or resinous residuum obtained by boiling down or distilling the turpentine of coniferous trees. It is a vegetable substance originality. The term mineral pitch has been applied to the purer forms of asphaltum that resemble in appearance the black pitch of the apothecaries. The Germans also use the term "glance pitch" to designate those very pure and hard varieties of asphaltum that break with a brilliant, glistening fracture, resembling obsidian more nearly than the less pure varieties of asphalt. This use of the word pitch, specialized as mineral pitch, as equivalent to asphaltum, while having little to recommend it, was not particularly objectionable until it became gradually applied to a great variety of substances, many of which are the same by-products of manufacture al-

luded to above. These artificial by-products have also been called artificial asphaltums and asphalts, and in some instances artificial bitumens. They are solid residuums obtained from the distillation, usually destructive, of coal tar, blast-furnace tar, coke oven tar, candle tar, California petroleum, maltha, etc.*

Reference has already been made to the distinction made by Dr. Hunt between coals and bitumens by the use of solvents. The natural bitumens are not as readily to be distinguished as pyrobitumens from the pitches or artificial bitumens so-called, as the latter are miscible with nearly equal facility in nearly all the menstrua that dissolve natural bitumens. They are, however, more easily to be distinguished by chemical tests and are in no manner equivalent to each other. The artificial bitumens, so-called, possess far less chemical stability in the atmosphere than natural bitumens. Mr. Clifford Richardson has very happily chosen the name "residual pitch" to designate these products of destructive distillation.

The word bitumen may, therefore, be strictly defined as a generic term that is used to designate a class of minerals as they occur in nature, that are soluble in chloroform and other neutral liquids. They all consist principally of compounds of carbon and hydrogen, but often contain compounds of nitrogen, sulphur and oxygen, and in the solid forms, compounds of iron and alumina. The species under bitumen occur in the gaseous, liquid and solid states and in mixture with solid minerals to form rocks.

This work is devoted to a discussion of the solid forms of bitumen and their uses in the construction of pavements.

*Paving & Municipal Engineering, 1894, Vol. vii, p. 310.

CHAPTER I.

THE GEOGRAPHICAL DISTRIBUTION OF SOLID AND SEMI-SOLID BITUMENS AND BITUMINOUS ROCKS.

In the valley of the Connecticut River solid bitumens have been observed filling thin seams and veins in eruptive rocks.*

In the eastern portion of the state of New York, in the region of eruptive and metamorphic rocks, veins occur similar to those reported from Connecticut.† In some of the cavities of the New York limestones the crystals which line them are covered with a substance, black and shining, with the fracture and appearance of anthracite.

Veins occur in the trap of New Jersey filled with a bituminous mineral.‡

In Ritchie county, West Virginia, on McFarland's Run, a small tributary of the south fork of Hughes River, which enters the Little Kanawha, is found a vein of bituminous material, called asphaltum, and named Grahamite, which is no doubt closely related to other forms of bitumen, but in precisely what manner, has been a subject of much controversy. The vein cuts the nearly horizontal sandstone strata nearly at right angles and stands vertical to the horizon. Very extensive mining operations were commenced upon the vein, but the mass was soon worked down to the lower level of the sandstones, and was found to pinch out in the shales beneath. It presented all of the phenomena of an eruptive mass. The material was found to be very valuable for enriching illuminating gas, for which it was chiefly used; but a thickness of several hundred feet of shale, in which it was almost entirely wanting, prevented continuous working, and the mine has long been abandoned. Other smaller but other-

*J. C. Percival on "Indurated Bitumen." *Geol. of Conn., Am. Jour. Science* (3), xvi, 130.

†L. C. Beck, *Am. Jour. Science* (1) xlv, 335.

‡L. C. Russell, *Am. Jour. Science* (3), xvi, 112.

wise similar veins occur in the neighborhood. From a visit made to the Grahamite deposit in 1881 and a very careful examination of the locality in company with several of the men who helped mine out the deposit, the author concludes, after several hours' conversation with these men, that the only description of the occurrence of Grahamite that conforms to the observed facts is found in the report of Prof. Henry Wurtz, published in 1865. His observations were made while the mine was being operated. He says: "The general aspect of the mass, as well as all the results of a minute examination of the accompanying phenomena, lead irresistibly to the conclusion that we have here a fissure which has been filled by an exudation, in a pasty condition, of a resinoid substance derived from or formed by some metamorphosis of unknown fossil matter contained in deepseated strata intersected by the fissure or dike. It is not necessary to suppose a degree of fluidity greater than semifused pitch or inspissated tar. Such a soft doughy mass, though flowing but slowly, would in time be forced by a very moderate pressure into every portion and into every crevice of the fissure."*

In Texas, near the mouth of the Brazos River, and in other parts of Texas, beds of asphaltum occur, evidently resulting from the decomposition of maltha or petroleum.

In Montague County, on the south side of the Red River Valley, deposits are found of sand saturated with bitumen. While the mineral is, geologically speaking, a rock, the sand falls asunder when the bitumen is dissolved away from it. While the deposits are of considerable extent, they are not easily accessible and are only of local value.

A deposit of limestone impregnated with bitumen, of limited extent, occurs near the town of Burnet, Burnet County, Texas.

The most valuable deposits of solid bitumen in Texas are situated in Uvalde County. "The only deposit worked in this somewhat extensive field is that by the Uvalde Asphalt Co., 18 miles west of Uvalde and 8 miles southeast of Cline, a

*J. P. Lesley, *Proc. Am. Philos. Soc.*, March 20, 1863; Report on a Mineral Formation in West Virginia, Henry Wurtz, 1865; *Proc. Am. Assoc. Adv. Sci.*, xviii, 124, 1869; S. F. Peckham, *Am. Jour. Sci.* (2), xlviii, 362, 1869, and *Am. G. L. Jour.*, xi, 164; W. M. Fontaine, *Am. Jour. Sci.* (3), vi, 1873; I. C. White, *Bul. Geo. Soc. Am.*, x, 1898; Asphalt and Bituminous Rock Deposits of the United States, G. H. Eldridge, 1901, p. 232.

station on the Southern Pacific railroad, with which it is connected by rail. The material is a coquina, or shell limestone, saturated with bitumen into a solid mass. When the bitumen is dissolved with chloroform, the shells remain, connected together at their points of contact and containing in the cavities of the shells crystalline masses of rhomb spar and pyrite. I have examined a number of specimens from this locality and they are very nearly identical in their characteristics and very unlike any similar material that I have seen. Several other deposits in the vicinity, of similar material, but less accessible, have been discovered.

The bitumen itself has a brilliant lustre when fractured, but where, in the broken rock, that portion which formerly was in contact with the walls of the cavity it filled, is exposed, the brilliant lustre is wanting, a surface of dead black replacing it. The bitumen, when extracted, is hard and brittle and at the same time flexible. In hardening in the rock it apparently suffered no shrinkage. The asphaltic limestone itself is tough and unyielding.

Bitumen occurs in a vein in the region of Upper Willow Creek, in the Middle Park, Colorado. The material resembles Gilsonite and has been injected into a fissure vein.

In that portion of Utah adjoining the northwestern portion of Colorado, solid bitumens occur in great variety. Various names, as Wurtzilite, nigrite, etc., have been given to these varieties. The bitumens of commercial importance are those known as ozocerite, Gilsonite and bituminous sandstones. They are found in what is known as the Uintah basin, in which lies the valley of the Green River, and the streams that unite to form it. Gilsonite is a black solid of very brilliant luster and with a conchoidal fracture, and exceedingly brittle. When pulverized it forms a chocolate-brown powder. In the vein it exhibits the "pencillate structure that is observed in starch and other substances under pressure. It occurs over an area that extends about five miles east of the Colorado line westward for sixty miles into Utah."

"The larger veins are somewhat scattered, one lying about $3\frac{1}{2}$ miles due east of Fort Duchesne, a second in the region of Upper Evacuation Creek, and the two or three others of chief importance, in the vicinity of White River and the Colorado-

Utah line. Besides these, there is a 14-in. vein near the western edge of the area in the vicinity of the fortieth parallel; another of equal size about six miles southeast of the junction of the Green and White Rivers; a third in a gulch four or five miles northwest of Ouray Agency, west of the Duchesne River, and a number from 1/16 in. to one ft. in thickness in an area about ten miles wide, extending from Willow Creek eastward for twenty-five miles along the sides of the Green and White Rivers. The vein near Fort Duchesne has been worked longest, and has been opened to a depth of over 100 ft.

The most important locality of Gilsonite is the region immediately north of White River, near the eastern edge of Utah. Here are three nearly parallel vertical veins of almost constant N. 60° W. trend, cutting and extending slightly into the shales of the Green River below. The veins are known as the East and West Bonanzas and the Cowboy, the two Bonanzas uniting to the southeast. The two Bonanzas are at varying distance from each other, while from the East Bonanza the Cowboy is distant about 2½ miles. None of the veins were exploited, as recently as 1901, only a shallow prospect appearing here and there. In general features and in filling they are like the veins near Fort Duchesne and the material occupying them is unquestionably derived from the same ultimate source as that in the others. The Bonanza veins may be traced from the White River cañon northwestward for 7 miles. The Cowboy is the largest of the White River veins. Its maximum width is 18 ft., but it holds a width of 8 to 12 ft. for a distance of 3 or 4 miles and at least 4 ft. for nearly 6 miles. The total length is between 7 and 8 miles. These veins, like those of West Virginia, are characterized by containing "horses" or pieces of wall rock embedded in the asphaltic mass, showing that the mass was eruptive, semi-solid and plastic, not fluid, when it was forced into the fissure.*

Veins of Wurtzilite, nigrite, ozocerite and also beds of

*The Asphalt and Bituminous Rock Deposits of the United States, by George H. Eldridge, p. 340-350. S. F. Peckham, Am. Jour. Sci. (2), xviii, 362, Nov., 1869.

bituminous limestones and sandstones occur in the valleys of the Green and White Rivers in northeastern Utah.

Next in commercial importance to the deposits of Utah are those of Kentucky. They occur as sandstones impregnated with bitumen. They extend from near Garfield in Breckinridge County through Grayson, Edmonson and Warren counties to Russellville in Logan County. Another deposit is found in the northeastern part of the state in Rowan county. The sandstones are very hard and are reduced to a powder with difficulty. These sandstones have been exploited commercially to a limited extent, the stone having been crushed and used in street paving in Columbus, O., Buffalo, N. Y., and other cities. Bituminous sandstones also occur in eastern Kentucky, in Carter county. The deposits have not been proved commercially valuable.

There is a deposit of bituminous sandstone near Higginsville, Lafayette county, Mo. It has not yet been proved of commercial value.*

There are very extensive deposits of bituminous limestones and sands in the Chickasaw nation of Oklahoma, both east and west of the Washita River. The eastern deposits are mainly in or near the valley of Rock Creek, east of Dougherty, a station on the Gulf, Colorado & Santa Fe railroad. These deposits have been exploited by the Gilsonite Paving & Roofing Co. of St. Louis, and by others. On the west, the deposits are found in the prairies that border the southern and western slopes of the Arbuckle mountains. Large maltha springs and beds of impure asphaltum occur to the south and southwest of the town of Elk. The principal deposits that have been worked are near the village of Woodford where the Schneider Bros. and the Smiths made several openings in a deposit of bituminous sand that formed a sharp anticlinal arch extending across the country for several miles. The material is sand, held together by bitumen which is readily separated by boiling water. The bitumen, when separated, is a semisolid maltha of great tenacity and purity. In this neighborhood other deposits of minor importance occur, but they have not been worked on a commercial scale. In the

*Asphalt and Bituminous Rock Deposits of the United States, by Geo. H. Eldridge, p. 240-262.

center of the Choctaw nation, on the headwaters of Tenmile Creek, in the Impson valley, occurs the vein of bitumen resembling Albertite that is called Impsonite. It has not yet been made of commercial importance.* At Velma, Stephens Co., and near Springer, Carter Co., a very pure form of asphaltum has been found, and called Grahamite, but its resemblance to Grahamite is quite remote.

The deposits of asphaltum and bituminous sandstones of California are found in the immediate region of the Coast Range, and are distributed from Point Arena in the north to Los Angeles in the south. They occur on the east and west slope of the general range and at several points within. As at present known, they are confined chiefly to that portion of the range lying south of the Bay of San Francisco. The purer variety of asphaltum occurs in the vicinity of McKittrick in Kern county, at the eastern base of the mountains near Santa Maria, in the Grasiosa and Azufre Hills, and again six or seven miles west of Santa Barbara on the coast. Bituminous sandstones occur at Point Arena, on the north, and at several localities in the south, notably near Santa Cruz, San Luis Obispo, Los Alamos and Carpinteria.

The Santa Cruz district of bituminous sandstone lies about sixty miles south of San Francisco. The deposits occur from five to six miles northwest of the city of Santa Cruz, the more remote being the most extensively quarried. The properties are controlled by a number of private individuals and by the City Street Improvement Co. of San Francisco. Most of the quarries are opened near the summit of the Empire Ridge, which parallels the sea and which is a spur of the Santa Cruz mountains. The quarries of the City Street Improvement Co. are opened at two different horizons, several of the quarries having their floors about 100 ft. above those of the others. These bituminous sandstones are essentially an aggregate of minute to medium sized quartz grains, which in form are sub-angular to rounded. It is in the interstices of this rock that the bitumen is held to an extent of from 14 to 16 per cent of the average specimen. The rock varies, but on the whole is soft, crumbling in the sun, very tenaceous and

*Asphalt and Bituminous Rock Deposits of the United States, by Geo. H. Eldridge, pp. 262-320.

gummy to the touch. The color is black to brownish-black, weathering to gray on exposure to the atmosphere. The temperature of the atmosphere, according as it is cold or hot, renders the rock either brittle or soft.

These deposits are extensively quarried for use on the streets of San Francisco and other cities of the Pacific coast.*

Bituminous sandstone is scattered along the length of the Salinas valley and its tributaries for a distance of 50 miles midway of its length. The localities best known are reached from Metz, King City, San Ardo and Bradley.†

The San Luis Obispo district of bitumen bearing rocks embraces an area of about 80 square miles, south and southwest of the town of San Luis Obispo; it is coincident with the ridge of moderate height that separates the San Luis valley from the sea, and which is the southeastern end of the San Luis Range. The quarries of the region are chiefly distributed about the periphery of the San Pablo terrace, but not a few have been opened well within its border. Unopened deposits are exposed at many localities throughout the area. Some localities show barren rock alone, others a bed with only traces of bitumen; still others a rock enriched sufficiently to afford a product of first grade. Many of the quarries, however, have been long abandoned, and it is impossible to judge unerringly of their actual contents.

The quarries of the San Luis Obispo region embrace a score or more of openings of various sizes, many of which have long been idle. The rock itself is fine grained and even textured, and in the main consists of quartz, but with traces of the same feldspar-like mineral found in the Santa Cruz deposits. The grains are both sharp and round, and are apparently cemented by the bitumen alone. The per cent of bitumen is nearly 15, and the rock is one of the best in appearance to be found in California. It is black on first fracture, weathering gray to brown. It is tough and tenacious and its use as a paving material is said to be satisfactory. The area occupied by the deposit and the local variations in its per cent of bitumen are undetermined. The sandstone itself is continu-

*Asphalt and Bituminous Rock Deposits of the United States, by George H. Eldridge, pp. 379-407.

†Ditto pp. 407-412.

ous over a region of many miles, of which this is a local enrichment. The composition, coarseness, interstitial space, and cross bedding have all influenced the degree of impregnation with bitumen which the rock has undergone. From the relations of the enriched to the more barren portions, and of the latter to parts free from bitumen, the appearance is as though infiltration, after the accession of the bitumen, proceeded laterally along stratification planes, the mass of the flow seeking the channels that were freest. Similar phenomena are observed in Oklahoma.

The bituminous deposits of the Santa Maria district embrace two varieties: one a high grade black material, found in veins; the other an impregnated shale. The two varieties may be found in the same locality, but the veins are especially developed in La Graciosa Hills. In the sandstone they are particularly clearly developed and have the appearance of originating in cracks irregularly disposed through a mass of fairly coherent sand or sandstone.

In the western portion of Santa Barbara County, in an area of about 15 by 20 miles, lying between the San Rafael and Santa Inez Ranges, is the Los Alamos district, the principal deposits of which occur on the Sisquoc and La Laguna ranches. On one of the richer portions of the Sisquoc sandstones, the Alcatraz Co. has opened its quarry. The opening is in the southern face of a ridge, extending along its length several hundred feet. The rock exposed and quarried has a thickness of something over 100 ft., most of which is of good grade. The bitumen is said to be removed from the sandstone at the quarry by means of naphtha, in which it is carried by a pipe line to a landing owned by the company, on the ocean front near Gaviota. It is there, according to account, separated by distillation, the recovered naphtha being pumped back to the quarry for further use as solvent and conveyor. The distance between the quarry and refinery is about 35 miles. Other deposits of bituminous sandstone occur in the neighborhood.*

At More's Landing, six miles west of Santa Barbara, on the coast are found extensive deposits of asphaltum contain-

*Ditto, pp. 413-439.

ing varying amounts of sand. The bitumen occurs in veins which are exposed as the sand, forming the ocean bluff, is washed away. Originally large masses, that had a tabular form resting upon a sort of talus that extended into the sands below, were scattered over the bed of the ocean in front of this bluff, some of them above and others beyond low water mark.

Three or four miles west of More's Landing, and ten miles west of Santa Barbara, the noted La Patera mine was worked for several years on a vein of asphaltum that was more or less irregular and intermittent, the maximum width being 12 ft. The trend of the main vein is N. 30° E. with a nearly vertical dip. Lateral cracks extend in all directions. The several shafts of the mine descend to a maximum depth of 500 ft. Below the 100-ft. level the tendency of the bitumen to swell in floors of the tunnels, required its constant removal. It is stated that a body of bitumen equal to the length and breadth of the tunnel and 20 ft. high has been removed in one year. This swelling of the bitumen is accompanied with an escape of gas, which has produced a distinctively porous condition of the bitumen of temporary duration.

Fifteen miles east of Santa Barbara, at Carpinteria, on an ocean bluff, occurs another extensive deposit of loose sand saturated with a stiff maltha. The average thickness is about 12 ft. It rests upon the upturned edges of the shales which are filled with the holes made by bivalves so common in the bluffs along that coast.

Five or six miles east of the above named deposit near Punta Gorda veins of bitumen have been worked to a depth of 100 ft. Several veins of bitumen of varying purity have been exploited in the hills bordering the San Buena Ventura River to the north of the town of Ventura. None of them have proved commercially valuable.*

The Asphalto district lies in a semi-arid region on the western side of the San Joaquin valley about 50 miles west of Bakersfield. A careful examination of this locality was made by the author in July, 1894, during a visit of several days.

*Ditto, pp. 440-447.

The deposits of asphaltum were of two entirely distinct varieties. The first consisted of the residuum of an overflow of maltha which formed a sort of glacier which partially filled a cañon. Although the mass of this material was of enormous dimensions, covering an area of more than a square mile and many feet in depth at the center, the outflow was geologically recent, as human remains, and mortars and other utensils had been uncovered from the gravel at the bottom of the mass of asphaltum. The springs from which the maltha had flowed that furnished the material for the deposit, were situated high up in the hills, and the maltha had spread out in the dry season with overflows of dirt and rubbish when it rained until a vast mass of more or less impure asphaltum had accumulated in the cañon below. During the 18th and early part of the 19th centuries, when the entire country was used for grazing vast herds of cattle, the rancheros frequently set the surface of the maltha on fire to destroy the stickiness of the surface, as calves and sheep frequently lay down on the warm asphaltum and becoming glued to the surface, starved to death. These fires must have produced a very intense heat, as beds of coke or cinders twelve inches in thickness are found intercalated with the asphaltum. Notwithstanding so much has been damaged or destroyed there are thousands of tons left in good condition in the glacier-like mass of the outflow.

The second form in which the asphaltum occurs is in veins that outcrop in lines miles in length upon the sides of the almost barren hills. At the time of my visit several shafts had been sunk to a depth of about 90 ft. The veins were encountered in the galleries from 2 to 6 ft. in thickness, readily cleaving from the soft argillaceous sandstone which enclosed them. Since that time some of the shafts have been sunk much deeper, one of them to a depth of 300 ft. At this depth the teeth of a fossil horse were found enclosed in the asphaltum. At the time of my visit, in mid-summer, the temperature in the mine, at a depth of 90 ft., was sufficiently high to soften the bitumen in large masses. No water was encountered at that depth, and I have understood that none had been reached at the greater depth. The aggregate amount of bitumen in these hills seemed enormous; but very conflicting statements, some of which have represented the

deposits as worked out, have been given as a reason why the mines are no longer worked. The true reason is, probably, wholly commercial.

The out-crop of the veins and for some depth below the surface is decomposed into a brown friable mass, that on drying breaks into approximately rhomboidal masses resembling siderite. At a varying depth this brown material passes into black cohesive asphaltum. At the time of my visit the asphaltum averaged, from samples taken from the shafts by myself, nearly 90 per cent pure bitumen. All of the specimens contained alumina and iron in organic combination with the hydrocarbons, and a small percentage of hygroscopic moisture.

In British North America there are enormous deposits of bituminous sand in the valley of the Athabasca River. In New Brunswick the well known deposit of Albertite in the valley of the Peticodiac River in Albert County, was mined for many years. The material is a clean, pure asphaltum, jet black in color, with a brittle, conchoidal fracture. It was used as a crude material for the manufacture of illuminating oils, for which purpose it was found to be very valuable, until the discovery of petroleum in Pennsylvania rendered its manufacture unprofitable. It has never been used in paving.

In the English West India Islands of Barbadoes and Trinidad very extensive deposits of solid bitumen are found. The "munjack" of Barbadoes is a very pure, brittle, black asphaltum. On the Island of Trinidad the celebrated "Pitch Lake" furnishes the well known Trinidad pitch in vast quantities. As it occurs in the lake it fills a circular depression, known to be more than 100 ft. deep in the center, and covering an area of 114 acres. It has been suggested by Mr. Clifford Richardson that the bitumen fills the crater of an old mud volcano. There are many phenomena observed that render this suggestion plausible. The bitumen is in constant motion, rising in the center and falling at the sides, suggesting a slow ebullition. Copious springs of mineral water accompany the bitumen, and, saturating the mass, renders it plastic while at the same time large volumes of gas escaping in huge bubbles render the mass porous. For this reason the mass within the lake is called "cheese" pitch. On the northeast side the rim of the lake has been broken down and the pitch has

flowed out, and downwards to the sea in a vast flood plain of unknown depth and spreading like a fan it covers several thousand acres. For commercial reasons this overflow pitch has been called land pitch, although there is no essential difference in the clean pitch wherever it is found. The pitch is a unique substance. Nothing in the world resembling it is known to the author. It consists of bitumen, intimately mixed with organic salts of alumina and iron with iron pyrites and silica in a very fine state of division, the mass containing a variable amount of water. When a mass is laid in the sun the surface dries out and melts, forming a film that prevents further evaporation, the color changing from brown to blue-black. The surface of the lake and overflow will support a loaded team if kept in motion, but will yield to the weight of a man if he stands still for a short time. It is estimated that the lake and overflow contain several million tons of pitch. Bitumen resembling munjack is also found on the island of Trinidad.

On the main land of Venezuela, west of the bay of Paria in the state of Burmudez, extensive deposits of asphaltum occur, also in the western part of Venezuela on Lake Maricabo and the Magdalena River other extensive deposits are found.

In the island of Cuba, veins of asphaltum of large extent have been known for many years. Extensive deposits of asphaltum of great purity are also known to occur under water in the harbors of Havana and Cardenas. There are also extensive deposits of asphaltum at several localities in Mexico, near the coast of the Gulf of Mexico in the states of Tamaulipa and Vera Cruz. Dr. J. P. Kimball described in 1876 a vein of asphaltum as a deposit of Grahamite known as the Cristo Coal Mine.*

Deposits of very pure asphaltum occur in Egypt. There are no others reported from the African continent.

There are a number of localities in Europe-Asia, some of which are commercially of great importance. From an immemorial period very pure asphaltum has been cast up on the shores of the Dead Sea. Formerly it entered the commerce of that region, but for some years the amount obtained

*Private Report, New York, May, 1876.

from this source has been decreasing until it is no longer of importance. Asia Minor, Persia and the regions that border the valleys of the Euphrates and Tigris Rivers abound in deposits of solid bitumen, locally valuable. Extensive deposits are reported to exist in the mountains of Albania. Extensive quarries of bituminous rock are found at Ragusa in the island of Sicily, also at Limmer in Hanover. The most important deposits of bituminous rock in Europe are those of the upper valley of the Rhone at Pyrimont and Seyssel. The most valuable rock is a chalk saturated with bitumen, that is interstratified with sand and conglomerate that are also saturated. Eirinis d' Erynys, a Greek physician, published in Paris, in 1721, a pamphlet in which he described these deposits of sand and limestone saturated with bitumen that he had discovered some years before.* He further describes a bituminous distillate that he had prepared from this rock, which he used with very satisfactory results in the treatment of certain forms of disease. He compares these deposits to similar beds in the valley of Siddim near Babylon, and remarks that the mine of asphaltum is for Europe a treasure that has been unknown to us from the beginning of the world. These deposits were forgotten for nearly a century and were then rediscovered. They have since become of great commercial importance. Other European localities furnishing asphaltum and bituminous rock are not of commercial value.

The geological age of the different deposits of solid bitumens is an interesting study. Beginning with the extreme eastern deposit of Albertite it is found in a region that abounds in beds of coal of vast extent in the true coal measures. Proceeding westward across the continent of North America, the vein of Grahamite found in West Virginia was also in the coal measures. Continuing westward to the Oklahoma the extensive deposits found there are also in the coal measures. The deposits of Gilsonite and allied bitumens of Colorado and Utah are in the Cretaceous as are also those of central Texas. The bitumens of the Coast Range of California are found in formations from the Cretaceous up to the Quaternary.

*Dissertation sur l'asphalte ou ciment naturel découvert depuis quelques années au Val-Travers, dans le comté de Neuchâtel par le sieur Eirinis d' Erynys, professeur grec et docteur en médecine, Paris, 1721. Asphaltes et Naphtes, par Isidore Huguenet, Paris, 1852.

The bitumens of Cuba are found in formations not older than the Cretaceous while those of the other West India Islands and of Venezuela occur in formations that are later than the Cretaceous.

The formations in which the Dead Sea lies are Cretaceous, with eruptive masses, indicating active volcanic action at a recent geological epoch.

The bitumen of Albania and the east coast of the Adriatic Sea is found in formations none of which are older than the Cretaceous. The important bituminous limestones of the valley of the Rhone are Cretaceous, while those of Hanover are Triassic.

From what has preceded, the conclusion may be reached that large accumulations of solid bitumens and bituminous rocks are found in nearly every member of the geologic series from the Silurian to the Quaternary, but that there have been three especially prolific periods of activity when solid bitumens accumulated and were forced into crevices which had rent the surface of the earth with explosive violence. These were first, at a period subsequent to the deposition of the Coal Measures; second, during the deposition of the Cretaceous or later; and third, during the deposition of the Tertiary or later. The bitumens of these three epochs are characterized by marked peculiarities that will be discussed under the general considerations relating to the chemistry of bitumens.

CHAPTER II.

THE ORIGIN OF BITUMENS.

The origin of bitumens has been a fruitful subject of speculation among scientific men for more than half a century. Generally speaking, the theories advanced fall into three classes, embracing those which regard bitumen as a distillate produced by natural causes, those which regard bitumen as the product of a peculiar decomposition of organic matter within the formations in which the organic matter is enclosed, making the bitumen in a sense indigenous to the rocks in which it is found, and those which regard bitumen as a product of chemical reaction, the latter class being subdivided into those which regard bitumen as a product of chemical change in natural substances of which carbon and hydrogen are constituents, and those which advocate a purely chemical reaction between purely mineral or inorganic materials.

Whatever theories are held with reference to the origin of bitumens, no distinction can be made in the different classes of bitumens, but all of the varieties, from natural combustible gas through naphtha, petroleum and maltha to solid asphaltum, must be included in one common source.

"The argument for a purely chemical origin of bitumen was first brought to the serious attention of scientific men, through the publication of a noted paper by the distinguished French chemist Berthelot in 1866.* Among others the most conspicuous advocate of this theory has been Mendeljeff, who read a paper on the origin of petroleum before the Chemical Society of St. Petersburg, of which the following is a résumé.

The appearance of springs of petroleum at the surface of the earth shows the tendency of those mineral oils to traverse by infiltration the different strata of the earth in reaching the surface, a natural consequence of their lower density as compared with water. The place where petroleum originates

*S. F. Peckham, Report on the Production, Technology and Uses of Petroleum. Reports of 10th Census U. S., 1885, x, p. 63.

ought then to be situated beneath the strata where the springs themselves are found. The beds furnishing the mineral oil belong in general to several different formations of the earth's strata. Thus, in the Caucasus, the petroliferous zone is found in the Tertiary; in Pennsylvania, in the Devonian, and even Silurian. The place of the formation of the petroleum ought then to be sought in other strata. The sandstones impregnated with petroleum have never exhibited the carbonized remains of organisms. In general, petroleum and carbon are never found simultaneously; but it is difficult to suppose that petroleum has resulted from the decomposition of animal and vegetable organisms, because it would then be impossible to represent the origin of petroleum without a corresponding formation of carbon. On the other hand, it is impossible to imagine the existence of great quantities of organisms in the epoch preceding the Silurian and Devonian. These reflections have led the author to the supposition that petroleum is in no place of organic origin. In speaking of the hypothesis of La Place upon the origin of the earth, in applying Dalton's law to the gaseous state in which all the elements constituting the terrestrial globe ought to be found, and taking into consideration their relative densities, Mendeljeff recognizes the necessity of admitting a condensation of metals at the center of the earth. Among these it is natural to presume iron would predominate, because it is found in great abundance in the sun, in meteorites and basalts. Admitting further the existence of metallic carbides, it is easy to find an explanation not only for the origin of petroleum, but also for the manner of its appearance in the places where the terrestrial strata, at the time of their elevation into mountain chains, ought to be filled with crevices to their center. These crevices have admitted water to the metallic carbides. The action of water upon the metallic carbides at an elevated temperature and under a high pressure have generated metallic oxides and saturated hydrocarbons, which, being transported by aqueous vapor, have reached those strata where they would easily condense and impregnate beds of sandstone, which have the property of imbibing great quantities of mineral oil."

This and other chemical theories are supported by great names and are based on the most complete and elaborate re-

searches; but they require the assumption of operations nowhere witnessed in nature or known to technology.*

The most conspicuous advocate of the theory that bitumens are a product of chemical reaction, by which marsh gas is converted into more condensed hydrocarbons, appearing as fluid, viscous, and solid bitumens is Coquand, who has written so fully upon the occurrence of bitumen in Roumania and Albania. He found mud volcanoes associated with the occurrence of bitumen in Sicily, the Appenines, the peninsula of Taman, and the plains of Roumania, and concluded that mud volcanoes produce petroleum and other forms of bitumen by converting marsh gas into more condensed hydrocarbons.

It may be said, in reference to this theory, that, in so far as it expresses the fact that maltha represents an intermediate stage in the transformation of some varieties of petroleum into asphaltum and recognizes the chemical relation existing between marsh gas and the different forms of bitumen, it is entitled to consideration; but, in the chemical processes of nature complex organic compounds pass to simpler forms, of which operation marsh gas, like asphaltum, is a resultant, and never the crude material upon which such decomposing forces act.†

Most conspicuous among the advocates of the theory that bitumen is indigenous to the rocks in which it occurs are Drs. T. Sterry Hunt and J. P. Lesley. These very eminent gentlemen based their views upon observations made in Canada, West Virginia and Kentucky.‡

Conspicuous among later writers who advocate this view will be found Jaccard, the Swiss geologist who wrote so extensively upon the bituminous deposits of the upper valley of the Rhone, Dr. Edward Orton, late geologist of the State of Ohio, and Dr. Charles F. Mabery. The last named gentleman stated his views at length* in a paper read before the American Philosophical Society, April 3, 1900, from which the following is quoted:

"Much as has been said on this attractive subject, a

*Bul. Soc. Chem. de Paris, 1877, 501. S. F. Peckham. Rep. 10th Census U. S., Vol. X, p. 61.

†Bul. Soc. Geol. de France, xxv, 35.

‡See Report on Petroleum, by S. F. Peckham, Reports U. S. Census 1880, x, 62.

broader knowledge of facts is necessary before definite conclusions can be reached. What is known forms the basis for only one explanation concerning the formation of petroleum, and that is, that it was formed from vegetable or animal matter by slow decay or breaking down from the complex forms of vegetable or animal life under the influence of natural forces, with no great elevation in temperature such as is necessary for distillation.

"Mendeljeff's theory of the formation from carbides at high temperatures, recently asserted with greater force on the basis of Moissan's work with the electric furnace, demands too many hypothetical assumptions, and has too little support on the basis of fact. To reason from the artificial formation of alloys and carbides in an electric furnace to the natural formation of petroleum containing nitrogen, sulphur and oxygen, in the form of hydrotheophenes, hydrochinolines, and phenols, demands a too broad reach of the imagination to make the connections.

"Bearing in mind the fact that petroleum may now be regarded as one and the same substance whatever its source, and that the deposits in different fields are composed of the same series, differing only in the proportions of these constituents, it must be admitted that it had one origin and one only. With reference to the series of hydrocarbons, it is immaterial whether its source was animal or vegetable, for under the influence of natural agencies it could have been formed as well from one as from the other.

"This question has been attacked on chemical grounds from the wrong direction. Because hydrocarbons of the marsh gas series, ethylene series or acetylene series at temperatures of decomposition form minute quantities of the aromatic series, or that hexahydroaromatic bodies are formed from the aromatic hydrocarbons by heating with hydriodic acid, to assume that these changes were produced by natural agencies and resulted in the formation of the hydrocarbons which now constitute petroleum, together with the other constituents of petroleum, ascribes to these natural agencies a direction of action and power that we do not know they possess.

"In considering present knowledge with reference to the

natural formation of petroleum, it seems to me that the following questions must be answered:

"(1) What is the chronology of petroleum; in what order were the deposits formed in different fields?

"(2) Were the least volatile constituents formed from the most volatile or the reverse?

"(3) What is a reasonable explanation of the formation of the other constituents of petroleum?

"The first question must be answered by the geologist.

"It is natural to assume that the limestones formed by the accumulations of the shell remains of animal life were deposited first from the ancient sea. The sand stones, as products of erosion from the older rocks, were deposited last. The question as to whether the different deposits of petroleum were formed in situ, or formed in other strata and by some natural agency transferred to their present location, has not, I believe, been satisfactorily answered by the geologists. In the case of the limestone petroleum, it would seem that it must have been formed where it is now found, as Hunt and Orton have ably maintained.

"The theory of distillation from some other strata is not tenable in the light of present knowledge of the constituents of petroleum. Neither could any known constituents of plants that could form petroleum be distilled, nor could the heavier portions of petroleum be distilled; the result would be only very volatile distillates and deposits of coal or graphite. In this condition deposits of petroleum should always be accompanied by coal, or with coal in the near vicinity.

"In the case of Pennsylvania and the allied southern Ohio and West Virginia petroleum, it would be a great discovery to connect these deposits with the coal formation, for then the source would unquestionably be vegetable growth, and would support the opinion that this was the source of petroleum of this class. It is reasonable to assume, as is now believed, that Pennsylvania oil was not formed in the sandstones, but found its way there by natural agencies from lower strata, probably the Devonian shales. The infiltration of the crude oil through sandstones, would have a purifying effect. It is quite probable that the very light yellow crude oils from the

Berea Grit and other sandstones were filtered a second time or more into their present positions.

"With reference to the source of the limestone oils, the evidence is all in favor of animal origin, and the same is true of California oil, although its formation is far more recent than that of the others. Texas petroleum has not been sufficiently studied in relation to its occurrence and composition, but it is evidently of more recent origin, like California oil.

"With reference to the second question, is it more reasonable to assume, for instance, that the solid paraffine hydrocarbons were formed from the lower members of this series, or that the lower members were formed from paraffine? On this point some experimental evidence may be brought to bear. Reichenbach obtained paraffine from both vegetable and animal organic matters. Engler obtained paraffine by the distillation of fish oil, as Warren and Storer had done many years previously.

"It is well known that paraffine breaks down very readily into hydrocarbons with lower molecular weights, but it is not possible to polymerize the lower hydrocarbons into the solid paraffine hydrocarbons. The tendency in cracking of any constituents of petroleum is toward the formation of the lower series and finally carbon in the form of coke. So far as experimental evidence and observation have shown the nature and relations of the hydrocarbons which compose the different series in petroleum, the conclusion is convincing that the lower members of the series were formed from the higher. A single break in the ring of a methylene is sufficient to form by the addition of hydrogen a paraffine hydrocarbon.

"In answer to the third question, as to the formation of the sulphur, nitrogen and oxygen compounds in petroleum, these bodies have not been built up synthetically, but are the products of decomposition of more highly organized constituents of organic bodies. It would seem that the small proportions of these bodies in Pennsylvania oil, as compared with the larger proportions in limestone oils and California oil, should be strong evidence in favor of a different origin, that Pennsylvania oil came from organic vegetable remains, which should permit of the small amounts of sulphur and nitrogen compounds found in this class of oils.

■

"But I think it can be asserted as a fact that the very large proportion of nitrogen in California petroleum, amounting to one-fifth or more of the total weight of the oil, can only be accounted for by accepting animal remains as the source of their formation. As a summation of what is at present known of the origin of petroleum, the following answers may be given to the questions propounded above:

"(1) Petroleum containing large proportions of the volatile hydrocarbons, especially of the series $C_n H_{2n+2}$, such as Pennsylvania petroleum, was formed from vegetable organic matter. The limestone petroleum and California petroleum was formed from organic matter of animal origin.

"(2) Cellulose, starch and other similar bodies in plants, and the fats and nitrogen compounds in animal bodies, by gradual decomposition with exclusion of air, gave first the heavier bodies found in petroleum, and by natural agencies during long periods of time, with no considerable rise in temperature, further decomposition included as products the hydrocarbons with smaller molecular weights.

"(3) The nitrogen and sulphur constituents of petroleum could only have been formed directly from or through the agency of animal organic matter."*

For the consideration of this subject we are greatly indebted to the profound and skillful chemical researches of Dr. Mabery. His conclusions, however, are based too exclusively on the results of chemical research upon petroleum alone. All forms of bitumen from marsh gas to solid asphaltum have a common origin and that origin should be discussed as a phenomenon of the cosmos upon which geology, technology, mineralogy and chemistry cast strong side lights, and together yield the testimony upon which conclusions may be based. The following is a general review of the subject:

In view of the general acceptance of the nebular hypothesis, it is unnecessary to establish the fundamental proposition that bitumens, as minerals, are properly considered in their relation to all the other mineral species that have been identified and described as together constituting the earth's crust.

*Proc. American Philosophical Society, xlii, 36.

The clear distinction of these relations has followed upon many years of research along several lines. It began more than a century ago with the famous discussion waged between the Plutonists and Neptunists, as to whether fire or water had been most active in producing the phenomena of rock building. Mineral silicates were then supposed to have crystallized from igneous fusion, and the deposition of sediments to have resulted only in amorphous, uncrystallized rock. The idea that heat and water together may have produced all of the phenomena that have been attributed to the action of either alone has been of slow growth; but may now be said to be pretty generally accepted, although there are those who refer to the action of heat and of pressure alone phenomena that are without doubt properly the resultant of the action of heat and steam under pressure.

The discussions that have proceeded along the three lines of geology, chemistry and mineralogy, have been mainly directed to an elucidation of the problems relating to the formation of the crystalline rocks. To determine, therefore, the nature of metamorphic action and the conditions under which it might take place, was the problem to the solution of which Bischof, Hunt, Delesse, Daubrée and several others of the most gifted chemical geologists of the last century devoted themselves.* These gentlemen first considered the reactions that according to known chemical laws must follow the cooling of a heterogeneous mixture of the elements composing the earth, in a state of gaseous fluidity, and at a temperature that rendered chemical combination impossible; in other words, a state of complete dissociation. It follows that the most infusible elements would first condense and form a solid nucleus around which would float an ocean, in a state of igneous fusion, of more fusible elements and compounds, while over all would hover an atmosphere containing all the nitrogen and oxygen, the free hydrogen, sulphur and allied elements, with the chlorine and other halogens. As the cooling proceeded the silicon would combine with oxygen and

*G. Bischof, *Chem. and Phys. Geology*, Cav. Soc. ed. T. S. Hunt, *Chem. and Geolog. Essays*. Delesse, "Essay on Pseudomorphs." *Ann. des Mines*, xlii, 509; xliii, 393, 415; xvi, 317-392. *Mem. Acad. de Scien. de France*, xvii. Daubrée, *Comptes Rendus de l'Acad.*, November 16, 1837. *Etudes et expériences synthétique sur le Métamorphisme*, Paris, 1859.

bases, forming both acid and basic silicates, which would constitute a solid crust. The hydrogen and haloids combining would form the haloid acids and the sulphur and allied elements would form oxygen acids, all the hydrogen being oxidized into water, which with the acids would be alternately condensed and evaporated, falling as an acid rain upon the surface of silicated rocks, which in turn would emerge from the ocean of water heavy with dissolved chlorides and sulphates, while an atmosphere dense with carbonic acid would help to maintain a temperature that would retard the cooling through vast cycles of geologic time, in the course of which, under conditions entirely different from any now known, vegetable and animal life would appear upon the earth, or, more properly, in the waters that covered the earth.

It is very evident that the chemical conditions obtaining in this remote geologic epoch, while not incompatible with the development of life, were, however, very different from those which have prevailed at any time since the advent of any of the higher forms of animals. We have a right to believe that at the dawn of life, of all the elements that enter into the composition of vegetable and animal tissue—carbon, hydrogen, oxygen, nitrogen, phosphorus and sulphur—nitrogen alone was wholly free. Carbon and hydrogen existed in combination with oxygen as carbonic acid and water. Phosphorus and sulphur were oxidized, and in combination with basic elements as salts. The excessive proportion of carbonic acid and aqueous vapor in the atmosphere gave to it the property of transcalesence, by which, while readily penetrated by heat from the sun, it refused to transmit this heat when reflected from objects at the earth's surface. This gave to the atmosphere properties similar to those of a greenhouse, by which so high a temperature was maintained during the coal period that semitropical plants flourished at the poles. At an earlier period, before terrestrial vegetation had removed the carbonic acid from the air, and before the surface of the cooling earth had lost its heat by radiation, the palæozoic (dawn of life) ocean and the land gave support to both vegetable and animal life, at a temperature that at the present time would destroy most organic forms.*

*W. H. Brewer, *Am. Jour. Sci.* (2), xli, 389.

The strata which form that portion of the earth's crust which has been referred to the palæozoic era, are of enormous thickness and are found in different parts of the world, to present aspects strikingly similar. Messrs. Hall, Billings and Dawson, in North America, Salter and Hicks in England, Angelin in Sweden, and Barrande in Bohemia, have shown that the forms of animal life in that early period were very closely related, if not identical, in these widely separated areas; yet, below these formations, which hold the remains of marine animals, in Bohemia and Sweden if not elsewhere, there is a "region of fucoids," of great thickness, carrying back the dawn of vegetable life to a still more remote epoch.* Throughout the last fifty years, successive discoveries of fossils in strata hitherto supposed to be destitute of organic remains, have carried the apparent dawn of life back through successive geological formations, until the azoic (devoid of life) rocks have ceased to be appropriately named, and Mr. Hicks, speaking of the Cambrian fauna of Wales, says, "Though animal life was restricted to these few types, yet at this early period the representatives of the different orders do not show a very diminutive form, or a markedly imperfect state; nor is there an increased number of blind species. The earliest known brachiopods are apparently as perfect as those which succeed them; and the trilobites are of the largest and best developed types. The fact also that trilobites had attained a maximum size at this period, and that forms were present representative of almost every stage of development, . . . blind genera along with those having the largest eyes, leads to the conclusion that for these several stages to have taken place numerous previous faunas must have had an existence, and, moreover, that even at this time in the history of our globe an enormous period had elapsed since life first dawned upon it."†

The formations that contain these earliest palæozoic forms of life are now found for the most part in a crystalline condition; yet, Dr. Hunt affirms, "the oldest known rocks are

*James Hall, *Paleontology of New York*, Vol. III, Introduction. Billings, *Am. Jour. Sci.* (2), xxxii, 232. Dawson, *Canadian Naturalist*, v. d. Reports Geological Survey of Canada, v. d. Salter and Hicks, *Proc. Geol. Assoc.*, Quar. Jour. Geolog. Soc., v. d. Angelin *Palaeontologica Scandinavica*. Barrande, *Bul. Soc. Geol. de France* (2), xvi, 529-545.

†Hicks, *Quar. Jour. Geol. Soc.*, May, 1872.

stratified deposits of limestone, clay and sands, generally, in a highly altered condition; . . . it is, however, quite certain that the advent of life in these oldest fossiliferous strata was subsequent to the period of chemical reactions on a cosmic scale.”* The manner in which these geological formations and parts of formations may have been rendered crystalline has been very exhaustively discussed by Dr. Hunt in his chemical and geological essays. He has shown how fully his conclusions, based almost wholly on theoretical considerations, have been confirmed by the experiments of Daubrée, who was led to investigate this subject, from observing that the action of the alkaline, thermal waters of the spring at Plombières, at a temperature of 60°-70° C., had in the course of centuries given rise to the formation of zeölites and other silicated minerals among the bricks and cement of the old Roman baths.† He further shows that at a temperature of 100° C. silicates are produced from a reaction between alkaline silicates and carbonates of lime, magnesia and iron. He says further, “Now the supposed mode of formation of the primitive molten crust of the earth would naturally exclude all combined or intermingled water, while all the sedimentary rocks are necessarily pervaded by this liquid, and are consequently in a condition to be rendered semifluid by the application of heat. . . . If now, we admit that all igneous rocks, ancient plutonic masses as well as molten lavas, have their origin in the liquefaction of sedimentary strata we at once explain the diversities of their composition. . . . The presence of fossil plants in the melting strata would generate carburetted hydrogen gases, whose reducing action would convert the sulphurous acid into sulphuretted hydrogen; or the reducing agency of the carbonaceous matter might give rise to sulphuret of calcium, which would be, in its turn, decomposed by the carbonic acid or otherwise. The carburetted hydrogen and bitumen evolved from mud volcanoes, like those of the Crimea and Baku, and the carbonized remains in the moya of Quito, and in the volcanic matters of the island of Ascension, not less than the infusorial

*Chemical and Geological Essays, ed. 1875, p. 2.

†Etudes et expériences synthétique sur le métamorphisme, par M. A. Daubrée, Paris, 1859, p. 98; Ann. des Mines (5), xiii, 227.

remains found by Ehrenberg in the ejected matters of most volcanoes, all go to show that fossiliferous sediments are very generally implicated in volcanic phenomena."* Again, he states, that "in a letter to Sir Charles Lyell, dated February 20, 1836, Sir John F. W. Herschel maintains that with the accumulation of sediments the isothermal lines of the earth's crust must rise, so that strata buried deep enough will be crystallized and metamorphosed, and eventually be raised with their included water to the melting point." Again Dr. Hunt says, "We conceive that the earth's solid crust of anhydrous and primitive rock is everywhere deeply concealed beneath its own ruins, which form a great mass of sedimentary strata, permeated by water. As heat invades these sediments, it produces in them that change which constitutes normal metamorphism. These rocks at a sufficient depth are necessarily in a state of igneo-aqueous fusion, and in the event of fracture of the overlying strata may rise among them taking the form of eruptive rocks."† He calls the effects produced by such invasion of eruptive masses, local metamorphism. From these extracts from several of Dr. Hunt's essays, it can be easily understood that a struggle has been in progress from the time of the oldest known rocks to the present, between the shrinking and wrinkling crust of a cooling earth and the thickening deposits of sediment accumulating from its erosion.

One Sunday in the early summer of 1866, the author, together with Dr. George L. Goodale, late of Harvard University, were stranded at a small hostelry, at the San Fernando Pass, near the old Mission of San Fernando, in southern California. The day was very fine and we chose a morning climb to anything the hostelry had to offer; so, mounting our horses, we rode to the eastward over the flood plain of pulverized rock that at some former period had poured out of the great cañon back of where the town of Burbank now stands. We climbed one of the spurs of the San Rafael range to the west of the cañon. We first passed over rounded hillocks of sandy soil which as we ascended became gradu-

*Essays, p. 8.

†Essays, p. 9.

ally merged into soft fossiliferous sandstone. After a time the effects of heat became manifest. The clam shells and fossil clams, of which there were cart-loads, appeared crystalline, and the iron in the sand was no longer green but red. The sandstones became more dense and the clays were silicated. At length the strata passed into a micaceous gneiss and finally we found the central core of the mountain to be a light-colored fine-grained granite. About half way up, Dr. Goodale found a vertebra of a whale half buried in the sandstone and still very perfect in form, while the author found a fossil pine cone that had evidently received some rough usage on the ancient beach. This cone contained some seeds that showed it to be closely allied to the nut pine of New Mexico. The mountain consisted wholly of Tertiary sediments that had been metamorphosed precisely as Sir J. F. W. Herschel had suggested in his letter to Sir Charles Lyell.

It is not alone through a study of the crystalline rocks that the chemistry of the primeval world is interpreted. By a comparison of the kind and amount of salts dissolved in the waters of the primeval ocean that are enclosed in palæozoic strata with the kind and amount of salts dissolved in the waters of the present ocean, Dr. Hunt has shown that from the earliest geologic time until the present, alkaline carbonates derived from the subærial decomposition of feldspar have been carried into the ocean by streams, and the calcium and magnesium in the ocean have been successively precipitated as carbonates, producing limestones and dolomites, while common salt and calcium sulphate have accumulated in the present ocean, the former in large excess. There is abundant evidence that this palæozoic ocean was hotter than the existing one, as well as more saline, while it is equally evident that during long intervals its sediments carried down vast quantities of the remains of vegetable and animal life. He further repeatedly has shown in what manner these sediments were influenced by the organic matters that were enclosed in them. In his essay on "The Chemistry of Natural Waters," he has shown that argillaceous sediments deprive waters of the organic matter in solution by forming a compound containing an organic radical. He says, "There is reason to believe that alumina is under certain conditions dissolved by

waters holding organic acids," and cites melite and pigotite as examples of the compounds formed. He further shows that organic matter in water reduces sulphates to sulphides, producing from soluble sulphates of lime and magnesia carbonates of the bases, with hydrogen sulphide, free sulphur, or a metallic sulphide; the hydrogen sulphide being converted by slow oxidation or combustion, followed by absorption of oxygen directly into sulphuric acid, which is again, when in contact with organic matter, reduced to hydrogen sulphide.

He says with reference to the water of palæozoic brine springs, "In the large amount of magnesium chloride which they contain, these waters resemble the bittern or mother-liquor which remains after the greater part of the sodium chloride has been removed from sea-water by evaporation. . . . The complete absence of sulphates from many of the waters points to the separation of large quantities of earthy sulphates in the Cambrian strata from which these saline springs issue; and the presence in many of the dolomite beds of the calciferous sand rock of small masses of gypsum, abundantly disseminated, is an evidence of the elimination of sulphates by evaporation. . . . The brines of the valley of the Allegheny River, obtained from borings in the coal formation, are remarkable for containing large proportions of chlorides of calcium and magnesium, though the sum of these, according to the examples given by Lenny, is never equal to more than about one-fourth of the chloride of sodium. The presence of the sulphates of barium and strontium in these brines, and the consequent absence of soluble sulphates, is, according to Lenny, a constant characteristic in this region over an area of 2,000 square miles."*

Among many other illustrations that might be given of these non-sulphated palæozoic waters, I mention one which was obtained from a boring on Great Manitoulin island in Lake Huron, at a depth of 192 feet. "After passing through the black slates of the Utica formation, and for 60 ft. into the underlying Trenton limestone. . . . it contained no sulphates nor barium nor strontium." Another palæozoic water of a very different character was obtained from a well bored

*Bischof, *Chem. and Phys. Geol.*, i, 337. Hunt, *Chem. and Geol. Essays*, p. 121, ed. 1875. *Am. Jour. Sci.*, March, July and Sept., 1866.

for petroleum at Bothwell, Ont., in 1865. "At a depth of 475 ft. from the surface, and probably at or near the base of the Corniferous limestone, a copious spring was met with, of very sulphurous water and a little petroleum." The water contained sulphate of calcium and sulphides of sodium and hydrogen. Waters apparently similar are pumped from several of the oil wells in the vicinity. "The sulphurous impregnation is doubtless to be ascribed to the reducing action of hydrocarbonaceous matter upon the sulphates which the waters contain."*

A brief examination of the superposition of the palæozoic and earlier formations of North America will show the Laurentian, embracing the oldest known rocks of the globe, outcropping from the coasts of Labrador to Lake Superior and over a large area in northern New York. Associated with this system is the Norian, which is characterized by a great development of opalescent feldspars. Above these are the Green Mountain series, an inferior part of the Lower Silurian, which corresponds wholly or in part to the Huronian system of Canada and the region about Lake Superior. Above these are the White Mountain series, which are Upper Silurian and perhaps Devonian. These formations constitute for the most part the rocks of Canada, New England, eastern New York and the eastern slope of the Alleghenies southward through New Jersey, Pennsylvania and Virginia. Speaking of these rocks, Dr. Hunt says, "In the oldest known of them, the Laurentian system, great limestone formations are interstratified with gneisses, quartzites and even with conglomerates. All analogy, moreover, leads us to conclude that, even at this early period, life existed at the surface of the planet. Great accumulations of iron oxide, beds of metallic sulphides and of graphite, exist in these oldest strata, and we know of no other agency than that of organic matter capable of generating these products.† . . . Bischof had already arrived at the conclusion, which in the present state of our knowledge seems inevitable, 'that all the carbon yet known to occur in a free state can only be regarded as a product of

*Essays, 158-163, ed. 1875.

†On the north shore of Lake Superior, I have found spherical concretions of graphite occurring in a rock that is apparently eruptive.

the decomposition of carbonic acid, and as derived from the vegetable kingdom.' He further adds, 'living plants, decomposed carbonic acid, dead organic matters, decomposed sulphates, so that, like carbon, sulphur appears to owe its existence in the free state to the organic kingdom.' As a decomposition (deoxidation) of sulphates is necessary to the production of metallic sulphides, the presence of the latter, not less than of free sulphur and free carbon, depends on organic bodies; the part which they play in reducing and rendering soluble the peroxide of iron, and in the production of iron ores, is moreover, well known."*

Rocks of the Lower Cambrian in Great Britain as well as in North America are well known to exhibit carbonaceous remains. Of the former it is said, "They occasionally hold flakes of anthracite, and small portions of mineral pitch exude from them in some localities." The rocks of the Malvern hills contain fucoids. In the Quebec series on the south shore of the St. Lawrence, Hunt describes the occurrence of a carbonaceous substance, "entirely distinct from coal, which occurs in fissures, sometimes in the interstices of crystalline quartz. It is an insoluble hydrocarbonaceous body, brilliant, very fragile, giving a black powder, and results apparently from the alteration of a once liquid bitumen."† Similar material often lines cavities in the limestone in Herkimer Co., N. Y., and not only sometimes encloses crystals of quartz, but is often enclosed in quartz crystals. These limestones are not crystalline.

Above these formations just mentioned, in the carboniferous formation of both Europe and North America, anthracite occurs in metamorphosed strata. In Wales, Belgium, the Alps and France, such phenomena are frequent. The coal deposits of Massachusetts and Rhode Island are enclosed in highly metamorphosed strata. Much of the material is more nearly graphite than coal. Both the coal and the enclosing strata are so distorted that the bedding is destroyed and the material appears in segregated masses.

In the trap dykes that have penetrated the sedimentary

*Essays, pp. 301, 302. *Am. Jour. Sci.*, 1871.

†Essays, pp. 382, 396. W. Hodgson Ellis, "Analysis of Some Precarboniferous Coals," *Chem. News*, lxxvi, 186, Oct. 15, 1897.

formations of the Connecticut valley and New Jersey, veins of carbonaceous matter occur. These dykes are intruded masses, no doubt formed by the igneo-aqueous fusion of sediments that contained organic remains.* Petroleum is reported to have been obtained in granite in a well drilled by the Pacific Coast Oil Co., east of the San Fernando Pass.

With the exception of the exudation of mineral pitch mentioned above, I have seen no notice that bitumen occurs in crystalline rocks, but always in rocks adjacent to or above them. There are vast areas of the palæozoic formations of North America that are not crystalline, that have been more or less subjected to the action of steam and pressure at temperatures that have made them more or less the subjects of metamorphic action. Some of these rocks contain bitumen and others do not. The limestones in the bluffs of the Mississippi River at Minneapolis and St. Paul contain in the cavities of their fossils crystals of pyrite and rhomb spar. They immediately overlie the St. Peter sandstone and are said to belong to the Trenton group. Similar limestones in southern Michigan contain bitumen, free sulphur and sulphates in large amount. In southern Kentucky and Tennessee the limestones are often coarsely crystalline and contain large encrinite stems that are silicified. These same rocks contain geodes lined with crystals of quartz. Other geodes contain sulphates of barium, strontium and calcium, both with and without bitumen. In other localities the rocks of this age are filled with bitumen widely disseminated in small quantities. These rocks often exhibit very slight evidence of the effects of heat, but frequently are found immediately above or upon crystalline schists.†

In Prof. James Hall's celebrated Introduction to The Palæontology of New York," he shows that the earliest palæozoic sediments were deposited in a current that moved from southeast to northwest. Later the current moved diagonally across them from northeast to southwest. These later currents represent a vast interval of time, during which material accumulated to a depth of tens of thousands of feet of

*L. C. Beck, *Am. Jour. Sci.* (1), xlv, 335. I. C. Russell, *ibid.* (3) xvi, 112.

†S. F. Peckham, Reports of the Tenth Census of the United States, Vol. x. "Petroleum," p. 63.

coarse sediments to the northeast in Canada, and growing finer diminished to the southwest in the Mississippi valley to a few thousand feet. If metamorphic action is due to the accumulation of sediments, whereby the isothermal lines of the earth's crust rise to meet the increased pressure, by consequence of which sediments are brought into a state of igneo-aqueous fusion, it is not difficult to explain why, at a period in the earth's history, when the condition of the earth's crust, the ocean and the atmosphere, all contributed to maintain a high temperature, the strata as we pass from the southwest in the Mississippi valley towards the northeast should present, at the surface, increasingly the effects of heat.*

Let us now turn to technology and see what the experience of more than half a century can teach us in relation to this question of the origin of bitumen. Soon after 1830, Reichenbach in Germany,† Sèlligue in France and Gregory in Scotland, all worked upon the destructive distillation of pyroschists, wood, coal, peat and petroleum. They all discovered paraffine, and what is suggestive, they all propounded the idea that bitumens are distillates. They established the fact that pyroschists, wood, coal, etc., when destructively distilled yield paraffine and the oils found in petroleum. Sèlligue established quite a valuable industry in France, using as his raw material the schists of Autun. About 1850, the Scotch paraffine-oil industry arose. The raw material was a shale, called boghead mineral, that was well known to contain fossil fishes. The distillate of this mineral closely resembled petroleum, and when petroleum was discovered in the United States in commercial quantities, the refineries on the Atlantic coast, that had been importing the boghead mineral, commenced to work petroleum with slight changes in their processes. At the same time, the albertite of New Brunswick was also being distilled on the Atlantic coast, while west of the Alleghenies cannel was being distilled at Cannelton, on the Kanawha River, in West Virginia; at Cloverport, on the Ohio River, in Kentucky; at Newark, O., and near Pittsburgh, Pa. The experiment of distilling oil from Devonian

*Nat. Hist. of N. Y., "Palaeontology," iii, 45-60.

†*Jour. für Chem. u. Phys.*, von Schweiger-Seidel, 1830, lix, 436. *Trans. Roy. Soc. of Edinb.*, xlii, 125. *Rep. of Pat. Inven.*, n. s., iv, 109 *Jour. des Connaissances Usuelle*, Dec., 1834, p. 285. *Dingler*, lvi, 40.

pyroschists was also made at Erie, Pa. They yielded fifty gallons of distillate to the ton. Without exception every one of these materials yielded paraffine, and when the petroleum obtained from Pennsylvania and West Virginia was used as a substitute it was found that it yielded identical products, and the coal-oil industry was quickly rendered unprofitable. In an attempt to utilize all available material, William Atwood, who was one of the most skillful technologists in coal oil, was sent to the Island of Trinidad, where a plant was constructed and an unsuccessful attempt made to prepare illuminating and lubricating oils from Trinidad pitch. The pitch furnished distillates very different from the paraffine products obtained in the United States.

During the last years, before the coal-oil industry ceased to be profitable, a number of patents were granted for improvements in this technology, mainly for improved methods of distillation. The aim of these inventions was to effect a uniform heating of the material by which a slow distillation at low temperatures would be promoted. The presence of steam, often superheated, was found to be at all times beneficial. While to produce gas from these materials, it was found necessary to thrust them into a retort heated to a high temperature, to produce oil, it was found, on the contrary, best to distill at the lowest temperature possible. The intermediate oils, too dense for illumination and too light for lubrication, accumulated in the refineries, until Luther Atwood discovered that by distilling them in such a manner that the vapors were superheated the vapors were "cracked" or "dissociated," and when they were condensed they were found to be of such a specific gravity that they could be used for illumination. This was the most important discovery ever made in the technology of bitumens, and when applied to the manufacture of paraffine petroleum it was of enormous value.

Soon after 1860, attempts were made to treat the bitumens of southern California by the same methods of distillation that were employed in treating paraffine oils, but all the results obtained showed that the processes were being applied to different materials and the results were different. These results all pointed to an excess of carbon and more unstable compounds. On analysis these crude oils were found to con-

tain a large percentage of nitrogen as compared with paraffine petroleums.*

Canadian petroleum had been known to contain sulphur and to be difficult to refine. When similar oils were obtained in large quantities about 1885, in western Ohio, the sulphur petroleums became a serious problem in the technology of bitumen, as it was commercially desirable to treat them in the same manner as the pure paraffine petroleums of Pennsylvania. During 1893 and 1894, the technology of California bitumens was again investigated. Destructive distillation when applied to these bitumens, resulted in the production of a large volume of gas and asphaltic residuums with a distillate consisting principally of unsaturated hydrocarbons. The crude oils were found to be allied to the crude oils produced in the Scotch shale-oil industry, as they contain a large percentage of nitrogenous basic oils.†

There were thus established among North American bitumens three great classes: those known as Pennsylvania oils, consisting of nearly pure paraffines, for which I have elsewhere proposed the name of Warrenite; those known as Lima oil, which together with the Canadian oils contain a notable proportion of sulphur compounds, for which I have proposed the name of Maberyite, and the California oils, which occur in great variety and, while containing sulphur, are characterized as nitrogen bitumens and for which I have proposed the name of Venturäite. There is also a class of bitumens not yet investigated that are found on the eastern slope of the Rocky mountains from Mexico to the Arctic circle. In Europe, the paraffine petroleums of Galicia appear to be quite distinct from the bitumens of the Caspian Sea. Technology has also divided bitumens into two great classes that are largely determined by geological occurrence. The great petroleum region of North America, which is by far the most important in the world, lies in the great palæozoic basin that surrounds the Cincinnati anticlinal; while the bitumens of California, the West Indies and Europe issue from Tertiary rocks. These Tertiary bitumens are found in much greater

*S. F. Peckham, Reports Geol. Surv., California, "Geology," II, Appendix, p. 73.

†S. F. Peckham, Am. Jour. Sci. (3), XLVIII, 250.

variety and are uniformly more difficult to refine into commercial articles than the bitumens obtained from older formations.*

It is proper to mention in this connection three classes of investigations that have been made on a commercial scale. The first was made about 1860-65, by Cyrus M. Warren, and consisted in distilling destructively the lime soap made from menhaden (fish) oil. The products of this distillation were refined into illuminating oil, in all respects identical with coal oil and refined petroleum; and they were also proved by an elaborate research to contain the same constituent hydrocarbons. Quite recently, Prof. Karl Engler has repeated these experiments with the addition of pressure and steam during distillation. Warren's results were confirmed. Still more recently, Dr. S. P. Sadtler has discovered that the vapors escaping from linseed oil while being boiled furnish, when condensed, a petroleum-like liquid, which upon examination was found to consist of hydrocarbons identical with those found in Pennsylvania petroleum. It is an honor to American science that these results, valuable and interesting alike to science and technology, were obtained by American investigators.†

The general conclusion from technology appears to be, that for commercial purposes, crude bitumens and the products of their distillation may be duplicated by products of the destructive distillation of pyroschists, wood, coal, peat and a great variety of animal and vegetable substances.

It would be entirely unnecessary for the present purpose to notice in detail all the researches that have been undertaken upon bitumen, in all its various forms, since de Saussure published his paper on the "Naphtha of Amiano," in 1817. It is sufficient to indicate along what lines the investigations have proceeded and in what manner the results have

*Boverton Redwood, "Petroleum," etc., London. Charles Griffin & Co., 1896, ii. S. F. Peckham, Proc. Am. Phil. Soc., x, 445. Repts. 10th Census, U. S., x, "Petroleum," Am. Jour. Sci. (3), xlviii, 250 and 389, i, 33. Science xxiii, 74. Jour. Frank. Institute, Nov., 1895. S. P. Sadtler, Am. Jour. Pharm., Sept., 1896. C. F. Mabery, Jour. Frank. Institute, cxxxix, 401. Proc. Am. Acad. n. s., xxiii. Am. Chem. Jour., xix, 243, 374, 419, 796. B. Stillman, Jr., Am. Jour. Sci. (ii), (xliii), 242. Chem. News, xvii, 257. Bul. Soc. Chem. de Paris, 1868, p. 77.

†C. M. Warren and F. H. Storer, Mem. Am. Acad. n. s., ix, 177. Karl Engler, Berichte der Deut. Chem. Gesellschaft, 1888, xxi, 1816. xxii, 592. Dingler, Poly. Jour., 1889, p. 271. S. P. Sadtler, Am. Jour. Phar., Sept., 1896.

been interpreted. The earliest investigators analyzed bitumens as if they were homogeneous substances. They determined the carbon and hydrogen, added the percentages together and subtracted the sum from one hundred, calling the deficit oxygen. This went on for nearly fifty years. It is true that Prof. B. Silliman, Jr., fractionated petroleum by distillation, and queried whether the liquids that he obtained were educts or products. It was not until 1863 that Schorlemmer, in England, and Pélouze and Cahours, in France, published researches that professedly separated the compounds that were mixed together in petroleum. They were soon followed by Warren and Storer in the United States, who, by a superior method of condensation, succeeded in separating the hydrocarbons in coal-tar naphtha, naphtha from Pennsylvania and Rangoon petroleum, naphtha from lime soap of menhaden oil and also the hydrocarbons from oil of cumin. These researches established the existence in these liquids of several series of hydrocarbons, the members of which were identical, whether obtained from natural or artificial substances, and were also in many cases recognized as identical with chemical compounds already well known.*

Since these results were published, a great amount of work has been done with varying success upon a great variety of petroleums, in which work progress has been observed along two lines, viz., first, better methods of separation, and, second, better methods of ultimate analysis. It is only quite lately, however, that Prof. C. F. Mabery has succeeded, by distilling in vacuo with Warren's hot condenser, in so completely avoiding decomposition by cracking as to reach results that are final. While this is said without any wish to disparage the work of other investigators, it must be said with a proper regard for truth.† There is, however, a vast amount of chemical research on record, a very complete

*Theo. de Saussure, *Ann. Chim. et de Phys.* (2), iv. 314-320. London Jour. of Sci., iii. 411. B. Silliman, Jr., *Am. Chemist*, ii. 18. *Moniteur Scientifique*, No. 366. *Am. Jour. of Gas Lighting*, xvi. 83. *Wagner's Ber.*, 1872, p. 848. C. Schorlemmer, *Chem. News*, 1863, viii. 157; xi. 255. *Am. Jour. Sci.* (2), xxxvi. 115. *Rep. de Chim. Appliquée*, 1863, p. 174. *Jour. fur Phar.*, xxi. 320. J. Pelouze and Aug. Cahours, *Comptes Rendus*, lvi. 505; lvii. 62. *Ann. de Chim. et de Phys.* (4), i. 5. *Am. Jour. Sci.* (2), xxxvi. 412. C. M. Warren and F. H. Storer, *Mem. Am. Acad.*, n. s., ix. 121-176. *Am. Jour. Sci.* (2), xxxix, xi and xii. *Chem. News*, xii. 85, 261, et seq.

†C. F. Mabery, *Proc. Amer. Acad.*, n. s., xxiv; *Amer. Chem. Jour.*, xix, 243, 374, 419; *Proc. Am. Phil. Soc.* xlii, 36

résumé of which can be found in the exhaustive work of Boverton Redwood, which has given results sufficiently accurate for our purpose. These results may be generalized as follows:

The Pennsylvania petroleums are the purest paraffine petroleums known. They contain small percentages of olefines and traces of benzoles. The same hydrocarbons have been found in other petroleums, in the distillates from cannel coal, pyroschists, peat, wood tar, fish-oil soap, fish oil under pressure and linseed oil, and also from Grahamite, Albertite, ozocerite and many other substances of mineral and organic origin.*

The Lima and Canadian petroleums contain the paraffine series, with a notable proportion of sulphur derivatives of the paraffines, formed by substitution; and also traces of benzoles and nitrogenous basic oils.†

The Russian oils contain the benzole hydrides and naphthenes, with little, if any paraffines.‡

The California oils, so far as at present known, consist of the benzole hydrides, naphthenes, benzoles and sulphur substitution compounds with a large percentage of esters of nitrogenous basic oils, and no appreciable amount of paraffines.||

The Scotch shale oils contain paraffines, olefines, benzoles and esters of nitrogenous basic oils.**

These esters are also found in coal tar and in Dippel's oil, the latter being an oil obtained as a distillate from the gelatine of bones.

No satisfactory research has ever been undertaken upon semi-fluid malthas or solid asphaltums. They cannot be distilled without decomposition, and no analysis by solution has yet been made that was not highly empirical. It is assumed, rather than proved, that many solid bitumens contain oxygen.

*Schorlemmer, Pelouze et Cabours, Warren and Storer, Mabery, loc. cit.

†Mabery and Smith, Proc. Amer. Acad., n. s., xxiii; Amer. Chem. Jour., xvi, 83, 89, 544; xvii, 713; xix, 419.

‡S. F. Peckham, Proc. Amer. Phil. Soc., x, 445; xxxvi, 154; xxxvii, 108; Amer. Jour. Sci. (3) xlviii, 250. C. F. Mabery, Jour. Frank. Inst., cxxxix, 401; Proc. Am. Phil. Soc., xlii, 36. Boverton Redwood, Petroleum, i, 203.

||Bellstein and Kurbatow, Ber. d. D. Chem. Ges., 1880, p. 1818. Jour. Amer. Chem. Soc., xlii, 232. Markonikow and Oglobini, Ber. d. D. Chem. Ges., xviii, 2284; Ann. de Chim. et de Phys. (6), li, 372.

**English patents.

They certainly do contain sulphur, and in some instances they contain nitrogen. When distilled upon a large scale solid bitumens are decomposed and nothing but decomposition products are found in the distillate, while coke remains in the still. These decomposition products are very varied. Those that are geologically old yield paraffine, while those that are recent do not.*

Prof. Mabery has remarked that all petroleums contain the same approximate principles in different proportion. While this statement may be absolutely true, it is not so relatively. The palæozoic bitumens have been most carefully studied and they consist mainly of paraffines. The Tertiary bitumens have been less carefully studied, and they consist principally of benzoles and their derivatives in great variety. Mingled with these are the olefines and other series of hydrocarbons in small proportion, with an immense number of oxygen, sulphur and nitrogen derivatives and substitution compounds, the existence of which has been only recently suspected.

It can, therefore, be asserted that the natural bitumens and the substances resembling them that are obtained by the destructive distillation of mineral and organic substances, are strikingly similar. The palæozoic bitumens bear a resemblance to the simple distillates produced in the presence of steam, at low temperatures, when nitrogen is practically absent. The Tertiary bitumens resemble the distillates obtained at higher temperatures and when the raw material is rich in animal remains. There are, however, a large number of bitumens that have been too little investigated to admit of any generalizations concerning them. In illustration of this statement, attention is called to the valuable papers of Prof. Henry Wurtz, in which he shows that many so-called native paraffines are probably olefines.† The author suggests that some of them may be the higher naphthenes, that have the same percentage composition as olefines. The solution of these problems awaits a vast amount of research.

In the preceding pages I have given an outline of the

*S. F. Peckham and L. A. Linton, *Amer. Jour. Sci.* (4), 1, 193. S. F. and H. E. Peckham, *Jour. Soc. Chem. Industry*, xvi, 424; H. Endemann, *ibid.*, xv, 871; xvi, 121.

†H. Wurtz, *Eng. and Min. Jour.*, xlviii, 25, 114; li, 326, 376.

views generally held by chemical and physical geologists concerning the chemical phenomena attending the cooling of the earth and its shrinking and contracting crust. To these I have added a resume of the technical and chemical knowledge we possess concerning bitumens. I shall now proceed to discuss, in the light of these facts, the occurrence of bitumens and the relation of such occurrence to their probable origin.

Leaving the problems of orography to the physical geologist for solution, there are a few suggestions to be made relating to these problems, that I have not seen anywhere mentioned. If we regard the dizzy heights of the Andes and Himalayas, or the profound abysmal depths of the Pacific as isolated phenomena, they appear on a scale of oppressive grandeur and immensity; yet these irregularities in the earth's crust reach a maximum of only about ten miles in vertical height, which is only one twenty-five hundredth or four hundredths per cent. of the circumference of the earth at the equator. The local foldings of a few hundreds of feet in disturbed strata are microscopic when compared with the earth's diameter; and yet we are accustomed to regard these plications of strata as the result of sudden movements in the earth's crust. This is a pure assumption. The period of time through which critical observations of geological phenomena have been made when compared with the time that has elapsed since life dawned upon the earth is also microscopic; it is a smaller fraction than four hundredths per cent. The element of time in geological phenomena is only just beginning to be appreciated. We have learned from a few years of observation that some continental masses are rising and others falling with reference to the sea level; yet no one has observed these movements through many centuries, nor have these vertical movements of the coasts of the world been correlated and the laws that govern such movements been determined. We do not know whether a continent has emerged from an ocean maintaining a constant level, or whether the ocean has receded as the contracting mass has rendered the ocean depths more profound, or, as is more probable, the shrinkage of the crust has changed the distance of the ocean surface from the center of the earth, rendering the elevations apparently greater. It is not material to this ques-

tion that we should know. Nor is it of importance to consider whether the continued operation of forces at present active through countless centuries, or the repeated interjection of cataclysms of world disaster, has brought the earth to its present condition. Volcanic eruptions, earthquakes and floods, separately and unitedly, change the face of nature within our own generation; it is reasonable to suppose that they have acted from the earliest period of the earth's history to the present time with constantly lessening violence. It is true that the local effects of such phenomena as the earthquakes at Lisbon and Java and the Red River fault appear cataclysmic; yet these effects are microscopic when compared with the dimensions of the earth, and may have been, nay, probably were the culmination of a series of movements that had been in progress for immense intervals of time. I therefore believe that in stating the causes of those changes that have taken place at the surface of the earth as we know it, one of the most important considerations is the unlimited periods of time through which the pressure due to accumulation of sediments and the consequent development of heat has acted upon those sediments, which in many instances were filled with water charged with mineral matter in solution. From the combined action of pressure, heat and steam, through unlimited periods of time, the constituent elements of sediments have been brought into every possible state of combination, from obsidian and pumice, which have been completely fused, through lavas, granites, gneisses, etc., to sediments in which there has been no change at all. As Dr. Hunt has fully shown, the action of thermal waters, which have been largely instrumental in producing these changes, has been often extremely localized, both laterally and vertically, and may be greatly varied by the constituents of the sediments themselves.

If then, we accept the hypothesis that all of the rocks as we now know them are sediments, whatever may be their present condition, we are forced to the conclusion that life first appeared upon the planet at a date too remote to be determined even in geologic time, and that the remains of organic forms have practically been a constant constituent of sediments from that time to the present. As might be expected, we find organic remains in every possible condition,

from crystallized graphite to unaltered cellulose. Vegetable and animal remains are found in every conceivable condition of replacement and alteration. We find pseudomorphism in the strictest sense as well as metamorphic action developed in every possible degree. Nor can we assert that any of the older strata are free from such action, for metamorphism is, as the word signifies, a change of form, and no limits can be assigned to such change in either time, place or degree that are not arbitrary. There can be no question that as sediments have accumulated slowly so these changes have progressed slowly.

Nevertheless, following upon long periods of quiet, there appear to have been periods of cataclysmic violence, as when the vast lava sheets that form the table mountain of the Sierra Nevada were poured out, not from a single peak, but from a whole range of peaks; when the whole of southern Colorado and northern New Mexico and Arizona were covered with lava sheets thousands of square miles in extent; or when the valleys of West Virginia were upheaved, the Oil Break formed and the mass of plastic Grahamite forced into the fracture; or when the basic rocks that form the mounds of iron porphyry in Cumberland and Foster, R. I., were thrust up from the deeps; and the trap dykes along the whole eastern borders of the Alleghanies were poured into fractures of local extent; or when the veins of Gilsonite and allied bitumens were poured into fractures in a plastic condition in Utah. But these convulsions that have brought basic porphyrys, basalts, trap dykes and local metamorphism to the surface, have in the physical and chemical operations of nature produced anthracites and anthracitic residues and not bitumens. Bitumens are not the product of the violence of volcanic or cataclysmic action, but of the gentler action of normal metamorphism exerted through long periods, during which the volatile bitumen has been distilled from sediments containing organic matter, and at the lowest possible temperature, without regard to time, as the sediments were pressed down to an isothermal that admitted first of their distillation and then of the conversion of the carbon residues into graphite.

Dr. Hunt has left hundreds of pages in which he has shown that the crystalline and eruptive rocks, as we know

them, are altered sediments. His argument is conclusive that the carbon that they contain is derived from organic forms. When discussing bitumens he shows, first, that the pyroschists do not, except in rare instances, contain bitumen, and are not in the proper sense of the word bituminous. Secondly, he shows that the pyroschists do not, "whether exposed at the surface or brought up by boring from depths of many hundred feet, present any evidence of having been submitted to the temperature required for the generation of volatile hydrocarbons." Thirdly, he shows that as the oil occurs in the limestone it could not have been distilled. He further shows that the Utica slate that is beneath the lower Devonian limestones is unaltered, and adds, "More than this, the Trenton limestone, which on Lake Huron and elsewhere has yielded considerable quantities of petroleum, has no pyroschists beneath it, but on Lake Huron rests on ancient crystalline rocks with the intervention only of a sandstone devoid of organic or carbonaceous matter.*

I have already shown that sediments become crystalline at very low temperatures and that the crystalline schists below the lowest stratified rocks contain abundant evidences of organic forms. Are we to suppose that there was no intermediate zone in which normal metamorphism died out and faded into unaltered sediments? We ought to expect to find the pyroschists in their normal condition. We ought to expect to find the coal altered or unaltered, according to its proximity to the heated area. We should not expect to find the carbonized remains of organic forms in rocks containing bitumen; for we cannot suppose that those beds that yielded the bitumen by distillation were suddenly plunged into a condition of igneo-aqueous fusion by which the organic constituents were instantly converted into anthracite and gas. As a general rule the process of conversion must have been as gradual as the progress of deposition. We cannot assume that in every instance the anthracite is the residue from a distillation of which the distillate was completely lost. Moreover, the example cited above, of observations in southern California, is a complete demonstration, occurring as it does in a region

*T. S. Hunt, *Essays*, p. 169, ed. 1875.

rich in bitumen, that the change from sediments to crystalline schists is progressive and involves the organic as well as mineral constituents of the strata.

If a traveler should leave Boston, Mass., and travel in a generally southwest direction toward San Diego, in southern California, he would encounter along his route a series of object lessons that would lead to but one conclusion. Whatever the age of the crystalline rocks of New England may be, they are certainly for the most part older than the Carboniferous. The small basin around Mansfield, Mass., extending into Rhode Island, which contains the anthracites of that region, is surrounded by crystalline rocks, and, indeed, the anthracite beds themselves are, as already stated, altered to a substance nearer graphite than coal. The coal slates contain only impressions of coal plants, and fossils of any description are extremely rare in the vicinity. Intrusions of trap are frequent, and cones of highly basic porphyries are thrust up through all of the crystalline sediments at several points. The change of form has been very complete in respect to every constituent of the sediments.

Westward around New Haven, Conn., the bedding of the sediments has not been so completely obliterated, but the change in the organic constituents has been quite as general. In the gneissoid traps of that region, thin veins of anthracitic material occur, which alone remain to represent the organic constituents of the altered sediments. Continuing our course southwestward the same changed condition is observed in the crystalline schists of Manhattan Island, and across the Hudson through northern New Jersey. Intrusions of trap, too, are frequent through all this region and the sole representative of the organic constituents of the sediments is anthracitic residues.

On the western slope of the Catskills, through eastern New York, the crystalline rocks which exist at varying depths below the surface are overlaid with sediments which are frequently imperfectly metamorphosed, and as one moves westward into central New York and northeastern Pennsylvania, while the coal beneath the surface is anthracite and the residues before mentioned that fill cavities in the limestone are anthracitic, still the surface rocks show less and less signs of

alteration. As the summit of the Alleghanies is reached and passed, the coal beds fade by insensible stages from anthracite into unaltered splint and cannel coals. The beds of slate also become beds of pyroschists, and the formations generally assume the aspect of unaltered sediments. On the western slope of the Alleghanies the surface descends much less abruptly than it ascends on the eastern slope. The dip of the formations is much greater than that of the surface, consequently the outcropping edges of newer formations are repeatedly encountered, until in western Pennsylvania and New York metamorphism has ceased to be a problem in surface geology. These surface rocks are, however, geologically all below the coal, which in eastern Pennsylvania is metamorphosed into anthracite. There is no arbitrary line that separates the unaltered from the altered strata. The successive formations have thinned out, and in general they continue to become thinner as we go southwest; but there is no anthracite between the crest of the Alleghanies and the mountains of Arkansas. Throughout the Mississippi valley, as we pass to the west, these formations outcrop and overlies each other precisely like the shingles on a roof, with the pitch reversed.

In the Bradford oil fields, in McKean County, Pa., the drill penetrates a bed of porous sandstone that lies enclosed in impervious unaltered strata. It contains a few shells and fish bones, but no other fossils. Like the surface rocks it lies sloping toward the southwest, the lower portion submerged in salt water, the middle portion filled with petroleum and the upper portion filled with gas, both originally under an enormous pressure. In Warren County, farther to the southwest, the drill reaches petroleum not in the McKean County sand, but in a different sand, higher in the series. Still farther southwest, in Venango County, the surface rocks are still higher in the series and the drill reaches petroleum in a pebble conglomerate that outcrops at the surface to the northeast. These pebble conglomerates, known as the "Venango Oil Sands," formed great riffles in the currents of the primeval ocean. They are several miles long and a few rods wide, level on the upper surface, and rounded on the under surface to a feather edge at the sides. One is above the other and they are covered, when they contain petroleum, with a solid, im-

pervious shell of silica, that the drill penetrates with difficulty. The uppermost of these conglomerates consists of spherical pebbles of yellow quartz, about as large as cranberries; the lowest consists of lenticular pebbles of very white quartz. In both cases the pebbles are cemented together at their points of contact leaving large open spaces. These conglomerates are sometimes replaced by coarse, porous sandstones; neither of these contain fossils of any kind. Still farther southwest, on Slippery Rock Creek in Mercer County, and at Smith's Ferry in Beaver County, another sandstone—the Berea Grit—that is barren where it occurs in Venango County, yields petroleum above the pebble conglomerate. If a line be followed farther to the left, across western Pennsylvania and into West Virginia, the outcrops of the formations would rise successively in the scale until the oil would be found in the Mahoning sandstone, which lies at the top of the lower productive coal measures. Since the development of the Lima oil fields the range of rocks holding the petroleum reaches in Ohio, Canada and Pennsylvania from the Lower Silurian, Trenton limestone, to the lower coal measures. These rocks embrace nearly the entire palæozoic formations of North America. Very few wells have been sunk below the petroleum-bearing sandstone, for the obvious reason that it involved a useless expense. One of the deepest wells ever drilled in the oil region of western Pennsylvania was Jonathan Watson's deep well near Titusville. This well went down through all of the oil sands and the Devonian shales beneath them, to a depth of 3,553 feet, when just as it was abandoned a hard rock was struck which was supposed to be the corniferous limestone, which is the oil-bearing rock of Canada. The interval between the oil sands and the bottom of the well was filled with Devonian shales, that underlie the Bradford oil sand and are supposed to extend from Allegheny County, New York, to central Kentucky and in fact to underlie the entire petroleum region that produces Warrenite—the pure paraffine petrolums. When "dry" or unproductive holes are drilled outside the productive areas, they pass, at the horizon of the oil sands, through a different rock, which is compact and incapable of holding petroleum. These underlying Devonian shales outcrop at Erie, Pa., and furnish there the material that on dis-

tillation yielded fifty gallons of distillate to the ton. Where this formation outcrops it is filled with fucoids and has yielded small petroleum and gas wells. The men who drilled Jonathan Watson's deep well stated that "the soap stone (Devonian shale) became harder as they went down, and was redder in color, in fact, had been burnt like brick." In a comparatively few localities, petroleum has been found saturating rocks that lie one above the other. The upper rock invariably yields the most dense oil. In 1881 I saw a well in West Virginia, from which the same walking beam pumped at every stroke oil of 27° from a depth of 255 ft. and oil of 45° from a depth of 600 to 700 ft.

I have never seen a specimen of graphite reported to have come from any locality between the crest of the Alleghanies and the Ozark uplift. This is an uplift of the palæozoic formation west of the Mississippi River, extending from central Missouri to central Texas. It resembles that of the Alleghanies, but is on a smaller scale.* The eastern slope is more abrupt than the western. The formations of the central portions, in Arkansas and Oklahoma, are highly crystalline, and graphite and anthracite are of frequent occurrence and are found on the western slope. On this slope also, but farther west, in unaltered strata immediately above the crystalline formations, bitumen occurs in enormous quantity and great variety. Over a large area in the northeastern portion of Oklahoma heavy petroleums are found only a short distance beneath the surface, and, as I am informed, below the coal. South of the Red River, in northern Texas, bitumens occur saturating horizontal beds of sand that are intercalated between strata of more or less solid limestone. North of the Red River, in Oklahoma, every rock formation that is at all porous appears to be filled with bitumen. As far as I have investigated it, the bitumen is uniform in kind and quality. It has saturated beds of sand, strata of sandstone and limestone, some of which are hard and crystalline, others magnesian and almost as soft as chalk, some of them without fossils, and some almost all fossils, and all of them conformable with the Upper Silurian and Lower Carboniferous rocks that

*J. C. Branner, "Former Extension of the Appalachians Across Mississippi, Louisiana and Texas," *Am. Jour. Sci.* (4) iv, 357.

enclose them. In one locality a sort of bituminous breccia occurs, of immense extent, consisting of fragments of limestone and quartzite cemented together with bitumen. In another an immense horizontal bed of sand, completely saturated with bitumen, is overlaid with 30 or 40 ft. of conglomerate that has been more or less penetrated with it.

Many of the beds north of the river are in very sharp folds that bring the strata to the surface nearly vertical, in eroded anticlinals that extend across the country in parallel lines, often many miles in length. What is of especial interest in this connection is the occurrence in the vertical limestones and sandstones of imperfectly saturated strata. The bedding varies from the thickness of paper to a few inches. The rock mass was usually most easily penetrated along the lines of the thinnest beds. Fractures which cross all these beds, including both the thin and thick ones, show the bitumen completely filling the thin beds and only partially penetrating the seams and the mass of the thicker cryptocrystalline strata. Nothing could more beautifully and clearly demonstrate the fact that the bitumen was not indigenous to these rocks, but had penetrated them while previously and as at present in their nearly vertical position.

Continuing our journey across the continent, bitumen is frequently encountered in positions contiguous to normal or local metamorphism, until we descend into the great valley of California, west of the Sierra Nevadas. Here the development of bitumen has proceeded on a scale of vast magnitude. On the western slope of the Sierras the region around Roseville, in Placer County, and the vicinity of the city of Stockton, are well known to be rich in natural gas.* There are localities on these slopes that have also furnished petroleum, but, as before stated, the bitumen deposits of California are principally found in the Coast Ranges, and the great interior valley, including the ocean area lying between the Santa Barbara islands and the main land. The richest deposits have been found in Ventura, Kern and Los Angeles Counties, on the border line that separates the Cretaceous from the Lower Miocene. None of the bitumen is found in crystalline rocks (un-

*W. L. Watts, "The Gas and Petroleum Formations of the Central Valley of California," 1894.

less in the single instance mentioned above); yet the evidences of both normal and local metamorphism, in strata not far distant from the bitumen-bearing rocks, are abundant. The late Prof. Eli W. Blake, Jr., once visited the Santa Barbara islands and afterwards described to me the cascades of lava that had descended from the volcanic cones in the center of the islands over precipices into the sea. Bitumen has exuded for more than a century from the unaltered strata, whose upturned edges form the bed of the ocean, between these islands and the main land. The Tertiary formations that constitute the bluffs of the coast east and west of Santa Barbara contain deposits of bitumen of enormous extent, and exhibit evidences of metamorphic action still in progress. Almost every large bluff from Point Conception to San Diego contains a solfatera, the action of which leaves the Miocene shales, originally rich in organic matter, devoid of a trace of carbon.

The best petroleum wells of Ventura County lie in the cañons of the Sulphur mountain, one of the foothills of the Coast Ranges. Other wells are similarly located with reference to these ranges.* None of them have penetrated crystalline rocks; yet the core of the Coast Ranges only a few miles east of the wells of the Pacific Coast Oil Co., as Dr. Goodale and myself found, is granite. Fragments of crystalline rocks are washed out of many of the large cañons that head in the main Coast Range back of the foothills in which the oil wells are drilled. Deep drilling is extremely difficult in this region on account of the fragile character of the rocks. It might be impossible to carry a well down through all the bituminous strata to the crystalline rocks, but the fact that they are altered Miocene sediments and exist at a comparatively short distance below the surface does not admit of any question. The evidences of metamorphism, through the agency of hot, silicated water, are found everywhere. The formations contain abundant remains of highly organized animals; and the bitumens which they contain consist of benzoles and naphthenes, without an "appreciable amount of paraffines, if any."† They also contain sulphur and nitrogen. They

*S. F. Peckham, Mineral Resources of the United States, "Petroleum in California," 1894.

†Letter of C. F. Mabery to S. F. P.

are evidently the products of the distillation of highly organized animal tissue, as an effect of the accumulation of sediments, and of metamorphic action upon unaltered sediments, through granite and gneiss to lava and pumice.

If we turn from North America to Europe-Asia, the testimony of the most eminent observers seems equally convincing. Daubrée was satisfied that the origin of the bitumen was found in metamorphism. Other French chemical geologists were equally well-grounded in this belief. As early as 1835, M. Rozet read a paper before the Société Géologique de France in which he discussed the occurrence of asphaltic limestone at Pyrimont. He says, "The bituminous matter is found equally in the calcareous rock and the molass that covers it. It is evident that the action introducing it into the two rocks is posterior to the deposition of the latter. The manner in which it is distributed in great masses, which throw their ramifications in all directions, joined in such a manner that the superior portions generally contain less bitumen than the remainder of the mass, indicates that the bitumen has been sublimed from the depths of the globe. . . . It may be objected that such basaltic rocks do not appear in all the extent of the Jura. To that I reply that they are found in the neighborhood, in Burgundy and in the Vosges and further, that in the changes in the surface of the soil, whether occasioned by fractures or by the disengagement of vapors, the plutonic rocks do not necessarily appear at the surface. Perhaps in the deep valleys of the Jura the basalts are of very slight depth. . . . In the Val de Travers, near Neufchatel, similar phenomena are observed."*

In 1846, S. W. Pratt associated the occurrence of bitumen at Bastennes with the eruption of ophite in the Pyrenees.† In 1854, Parran remarks concerning the occurrence of bitumen in the environs of Alais, "whatever be the origin of these substances, whether they be due to interior emanations from fissures of dislocation or to circumstances exterior and atmospheric, it is evident that there was during the Tertiary period an asphaltic epoch in relation to which it is convenient to recall the numerous eruptions of trachytes and basalts which

*Bull. Geol. Soc. de France (1), vii, 138.

†Quar. Jour. Geol. Soc., ii, 80.

characterize that period, and have probably acted by distillation upon masses of combustibles hidden in the bosom of the earth."* The anthracites of the Alps offer convincing proof that large amounts of organic matter have been involved in the metamorphic action that has prevailed in that region. In like manner the relation of the bituminous deposits of Galicia and Roumania to the crystalline rocks of those countries show the part that metamorphism has played in their occurrence.

No theory that refers the origin of the bitumen to any physical or chemical action that has prevailed on a cosmic scale can satisfactorily explain the differences that exist in crude bitumens. Mr. Phillips has added the testimony of chemistry itself to show the improbability of a chemical origin for bitumens on a cosmic scale. Dr. David T. Day has shown the reasonableness of an hypothesis which regards the bitumens of Pennsylvania as distillates, but his idea that the variation in the petroleum of that region is due to the effect of filtration is, in my judgment, hardly tenable. In Pennsylvania the darkest and heaviest oils are nearest the surface. The sulphur content of bitumen is too wide a subject to discuss here in detail; yet it may be said in general that sulphur enters bitumens by a secondary reaction between the bitumen and the sulphates dissolved in natural waters. The freedom of Pennsylvania petroleum from sulphur has already been shown to be due to the absence of sulphates in the natural waters of the region in which they occur. As has already been stated, Prof. Mabery has shown that the sulphur compounds found in Lima oil are sulpho-paraffines. This would naturally follow the reduction of sulphates by paraffines, the reaction being a double decomposition in which sulphur is substituted for hydrogen in the paraffine. Filtration would not be likely to remove such compounds from solution in the other constituents of the petroleum.

In his discussion of the "Occurrence of Petroleum in the Cavities of Fossils," Mr. Phillips has offered some ingenious but wholly unnecessary suggestions to account for the presence of a nearly solid bitumen in the cells of a coral reef uncovered in a quarry. Petroleum occurs in the rocks of the oil

*Ann. des Mines (5), iv, 334.

regions filling cavities of every description. Geodes, fossils, sandstones, pebble conglomerates, porous limestones, the Chicago dolomite, gravel, anything and everything that has a cavity or a pore, has been found saturated with it. Why? Simply because the enormous pressure under which the bitumen has accumulated in the crust of the earth has forced it there. When it has entered cavities like those in the coral reef described by Mr. Phillips, the diminished pressure and evaporation have resulted in the escape of the most volatile constituents. When the reservoir of the Bradford field was first penetrated, the pressure was estimated at 4,000 lbs. per sq. in. Whether or not this estimate was approximately correct, the pressure was sufficient to throw the well casing and piping out over the top of a derrick and land it in a meadow near by. A short time after the famous Karg well was struck near Findlay, O., I, myself, saw a pressure gage register 450 lbs. per sq. in. Burning gas wells in western Pennsylvania sent streams of flame into the air 80 ft. in height. Notwithstanding this accumulation of the facts of experience during many years, writers still ignore the tremendous significance of such phenomena, and speak of these deposits of bitumen as if they resembled a turn-over or an apple-dumpling laid away by nature. Gas cannot have been held under such tremendous pressure through cycles of geologic time in reservoirs of porous rocks, from which it has been filtering, as suggested by Mr. Phillips.

The complete inadequacy of all these arguments was never more fully set forth than in the language used by Mr. Phillips: "The movement of the oil through the rock displaced from the interstices in which it had originally collected would have been accelerated as the transition from solid organic tissues to liquid had been advanced." The decomposition of organic matter in situ could never have occurred under any conditions of accelerated pressure of even moderate amount. Action and reaction being equal the rocks must have been consolidated and capable of resisting pressure before the pressure could accumulate. These facts are themselves the strongest reason for belief that the bitumens were never formed in situ in the porous rocks that contain them, but were gradually accumulated in those porous rocks that had been previously overlaid

with impervious strata capable of resisting the enormous pressure until the reservoirs were penetrated by the drill. The fact that in the limestone some fossil cavities are filled while others are empty lies in the further fact, that the lines of shrinkage and other fractures penetrated some of the fossil cavities while others remained intact.

Upon this hypothesis, that bitumens are distillates, all of the variations observed in bitumens of different geological ages are easily explained. The earliest forms of animal and vegetable life are admitted to have been nearly destitute of nitrogen; hence when these forms accumulated in sediments, which, borne down by deposits above them, invaded an isothermal that admitted of their distillation, they must have been distilled, in the presence of steam, at the lowest possible temperature; they must have been distilled under a gradually increasing pressure, the extent of which depended upon the porosity of the sediments above them, up to the surface. They must also have been distilled under a gradually increasing temperature which would have been largely controlled by the pressure. While the temperature and the pressure would have in every instance been the least possible, with steam always present, these physical conditions would on account of the varying porosity and consequent varying resistance of the overlying mass have produced very great effects in some instances and very slight effects in others. As a consequence, we have in natural bitumens, as in artificial distillates, materials varying in density from natural gas to solid asphaltum.

If these distillates proceeded from materials that would yield paraffine, these permanent and stable compounds, from marsh gas to solid paraffine, remained in the receptacles that nature had provided for them until they were released by the drill. If, however, the distillates proceeded from sediments of a different geological age, containing animal and vegetable remains more highly organized, that would yield different series of hydrocarbons, with compounds of nitrogen, then a very different bitumen would be stored in these receptacles. Secondary reactions would convert these primary distillates into a great variety of substances. The contents of the original reservoirs, borne down and invaded by heat, might become involved in a second distillation at an increased pres-

sure and temperature. Fractures of these reservoirs from excessive pressure might lead their contents to the surface along lines of contact of strata or with water containing sulphates by which an originally pure hydrocarbon would be converted into a sulphur bitumen. A nitro hydrocarbon, reaching the surface under these conditions, might, by the combined action of evaporation and reaction with sulphates, pass through all the varying degrees of density from petroleum to maltha and become finally solid asphaltum, and this through the lapse of time and abundance of material on a scale of vast magnitude.

Such, then, is the "Testimony of the Rocks," along a line which spans the western continent. Nearly the whole of this line has been brought under my own personal observation. There is also reason for believing that a line might be followed in the eastern continent from the North Sea to Java that would furnish equally convincing proof. To this testimony is added that of chemistry, technology, mineralogy, and the chemistry of the cooling earth. Each supports and corroborates the other. We have no need to search for coke until we know that coke was formed. We have no need to assume, that in the laboratory of Nature high temperatures and rapid action were necessary to produce results, for which infinite periods of time and the lowest possible temperature were fully adequate.

Dr. Edward Orton read at Montreal, December 28, 1897, an address in which the author notes two very important observations. In speaking of Mendeljeff's chemical hypothesis, "It is hard, therefore, to see why, the whole world over, petroleum is entirely wanting in the Archean and exclusively confined to the stratified rocks. There is not an oil field in the world in rocks of Archean time." I pass this by without comment to notice his observation upon the gas wells drilled in Oswego and Onondaga Counties, N. Y., one of which penetrated a limestone that was found between the Potsdam sandstone and granite, and furnished a gas pressure of 340 lbs.; the other at a depth of 120 ft., in the Trenton limestone, gave the gas pressure of 1,525 lbs. Dr. Orton well says, "A rock pressure of 1,500 lbs. per sq. in. stands for, nay demands, a hermetic seal." Speaking of the Potsdam sandstone and the

dark limestone beneath it, he says, "The drillings brought from these horizons seem normal in every respect. Certainly there is no hint of any transformation by heat. 'The smell of fire has not passed on them.' There is no carbon residue. The bituminous products found in them cannot owe their origin to the usual form of destructive distillation."* It is not likely that the usual form of destructive distillation as illustrated in a gas retort has obtained anywhere in the operations of nature. I regard the penetration of granite beneath bitumen-bearing rocks as a most conclusive and unexpected support to the validity of the views herein set forth. The longer I study the subject and the wider my experience becomes, the less I am prepared to assert that any formula is capable of universal application. I would therefore suggest, that, as we now find them, bitumens are in some instances still where they were originally produced by a process of decomposition of animal remains, that is at present being illustrated on a small scale in the shallow bays of the Red Sea. Further, that other deposits contain primary distillates from the vegetable and animal remains enclosed in geological formations that have been invaded by heat, steam and pressure in past periods of the earth's history; and finally, that in some instances, as we now know them, bitumens have been transferred and stored by a secondary invasion of bituminous deposits by heat, steam and pressure. The details of these various movements await for their expression a vast amount of chemical and geological research by those who are to come after us.

I have quoted thus fully from Dr. T. Sterry Hunt for two reasons; with all his eccentricities, he was a man of untiring industry and a profound interpreter of the phenomena of nature in the light of experiment. Therefore, no writer of recent years has expressed views that are entitled to more respectful consideration. He is also more widely quoted by both American and European writers upon the subject of the origin of bitumens, especially as an exponent of the doctrine that bitumens are indigenous to the rocks in which they are found, than any other author.†

*Bul. Geol. Soc. America, ix, 93.

†Proc. Amer. Philos. Soc., vol. xxxvi, 103; vol. xxxvii, 108.

This discussion is directed mainly to the origin of petroleum. It applies with equal force to all primary forms of bitumen, whether gaseous, liquid, semiliquid or solid. The evidence is constantly accumulating where bitumens occur in all parts of the world. In Texas the petroleum occurs in sands that are interstratified with strata that contain at a depth of only 1,200 ft., warm artesian water. During a recent visit to New Brunswick the author learned that anthracite had been discovered in the western extremity of the range of hills in which the Albertite occurs, and that petroleum had been obtained from wells drilled at a point lying between them. The entire region is a region of metamorphic rocks, changed through the action of hot silicated water.

The origin of bitumens cannot be established in laboratories, but must be wrought out as the result of a careful comparison of the operations of technology with the operations of nature, into which time has always entered in sufficient quantity.

CHAPTER III. THE CLASSIFICATION OF BITUMINOUS SUB- STANCES.

A correct classification of bituminous substances divides them into three classes, viz.: bitumens, pyrobitumens and factitious or artificial bitumens.

The first embraces those natural substances defined by numerous authorities as consisting principally of carbon and hydrogen, and occurring under gaseous, fluid and solid forms as natural gas, petroleum, maltha, and asphaltum or asphalt, sometimes pure and sometimes mixed in varying proportions with other substances. They occur in outflows, saturating beds and masses of rock and in true veins into which the solid forms have been injected in a plastic condition. They are more or less soluble in various neutral liquids, but particularly in chloroform and bi-sulphide of carbon. They are usually black in mass and brown in powder or solution, and are very inflammable.

In one of the earlier papers of Dr. T. Sterry Hunt it is shown that certain relations exist between coal and bitumens. Dr. Hunt read a paper at Terre Haute, Ind., in 1870, on the "Oil-bearing Limestone of Chicago," and later papers, in which he makes clear the distinction between minerals that are true bitumens, soluble in chloroform and bi-sulphide of carbon, and minerals that are insoluble in those liquids, but which yield, when distilled, substances that resemble bitumens in physical properties. These he called pyro-schists, and pyro-bitumens. This distinction he deemed of great importance, as it really is, and he enforced it with all the energy of which he had no lack. All coals, except anthracite, yield bituminous products on distillation. Besides the coals, there are deposits of carbonaceous minerals in great variety of form and degrees of purity that are known in mineralogy as bituminous schists and shales that also yield bituminous distillates. These are properly referable to the second class.

To the third class are referable an immense number of substances, most of which are by-products of manufacture, but some of which are direct products of the arts. They are properly divided into three groups, one of which consists for the most part of educts, obtained at low temperatures, the other of products, resulting from destructive distillation at high temperatures. A few are by-products of chemical reactions, which are referred to the third group.

Concerning this subject, three notable papers have lately been published that deserve the serious attention of chemists and technologists throughout the civilized world. I refer to:

First, "The International Association for Testing Materials, Brussels Congress 1906, Report on Problem 34; Fixing a Uniform Definition and Nomenclature of Bitumen, Presented by the Chairman of the Commission 34, Professor Dr. G. Lunge, with an Appendix; Investigations of Asphalt, by G. Lunge and V. Krepelka, translated by E. Ormond, Zurich." While this translation is very free, and sometimes incorrect, I have not observed many serious deviations from the meaning of either the French or German texts, with which I have made a careful comparison.

Second, "Beitrag zum Nachweis von Verfälschungen im Naturasphalt, von Dr. H. Köhler, Perth Amboy, N. J." This paper was published originally in the "Chemiker Zeitung," 1906, 30, No. 5.

Third, "Beitrag zum Nachweis von Verfälschungen im Naturasphalt, von Dr. Köhler, Betriebs-direktor der Rütgers-wirke-Aktiengesellschaft, Berlin." This paper was also published originally in the "Chemiker Zeitung," 1906, 30, No. 54.

A critical examination of each of these papers will be indulged and then such general discussion and conclusions will follow as the occasion appears to warrant.

Professor Dr. George Lunge, who is chairman of Commission No. 34, is the well known author of several works relating to the alkali and sulphuric acid industry, and also of a general work on Technology, the portion of which relating to bitumen was written by Prof. Dr. D. Holde, of the University of Berlin.

Dr. Lunge was appointed chairman of a very able com-

mission, consisting of Vice-Chairman Dr. Jenő Kovács, Tartsos, Hungary (deceased); and members:

Dr. M. Albrecht, Hamburg; Dr. L. Eger, Munich; Prof. Dr. D. Holde, Berlin, Vorsteher der Abtheilung für Ole am Königl. Material-Prüfungsamt. Gr.-Lichterfelde; Prof. Em. Paternò di Sessa, Rome, Senateur du Royaume d'Italie, professeur des applications de la Chimie à l'Universite de Rome; L. Schmelck, Stadtchemiker, Christiania; Dr. Max Böhm, Fabriksbesitzer, Privoz, b. m.-Ostrau; Prof. B. Kirsch, k. k. technolog, Gewerbemuseum, Vienna; Albert Grittner, Chef-Chemiker der kgl. ungar. Staatsbahnen, Budapest; A. W. Dow, Inspector of Asphalts and Cements for the District of Columbia, Washington, D. C.; Clifford Richardson, Asphalt Expert, New York Testing Laboratory, Long Island City, N. Y.

Quoting from the English translation of the report of Dr. Lunge above mentioned, "a circular in German, French and English was immediately addressed to the various members, in which the undersigned expounded his working program, and invited his colleagues to make him definite proposals founded on their own investigations, for a definition and nomenclature of bitumen." He further requested "to be informed of the different methods employed by them in analyzing and testing the different kinds of bitumen, to enable him to draw up a system of classification founded on these investigations. In order that it would be possible for him to carry out the control analysis in his laboratory during the summer term, he requested that the proposals be sent to him not later than May 1, 1903.

"In October, 1902, he together with one of his students, Herr V. Krepelka, began an experimental work on the methods of analyzing bitumen. This investigation was finished in the course of 1903.

"Unfortunately only a very few answers were received by May 1, 1903; the undersigned therefore issued a second circular in three languages, requesting replies on or before November 1, and finally a third on November 20. * * *

"The undersigned did everything in his power to push forward the work entrusted to him, but the result attained

was very small, notwithstanding an extensive correspondence in three languages in addition to the circulars.

"Very few answers were received although a second and third request were sent out. Dr. Albrecht, Dr. Eger, Engineer Locherer and Mr. A. W. Dow did not reply at all. Letters from Dr. Holde, L. Schmelck, A. Grittner, Profs. Kirsch and Paterno did not contain any important information. Mr. Richardson wrote fully and gave detailed information regarding American asphalt and the methods used by him in analyzing the same. He prepared between three and four hundred pages of manuscript, 'but feeling that his results were not such as could be placed before our commission, he declined to make any report.'"

Only two opinions on this subject of any importance to the commission were received, one from Dr. Jenő Kovács, and the other from Dr. Max Böhm.

Dr. Kovács (who was the Vice-Chairman of the Commission, now deceased, and who was an asphalt expert of the highest rank and a voluminous author on the technology of bitumens), states "that he understands under 'asphalt' only those materials consisting of or containing asphalt bitumen, the bitumen of which has resulted from natural resinification or oxidation. The materials which he divides into the following classes,—asphalt-bitumen, asphaltic stone, asphaltic sand, asphaltic mastic, liquid asphalt, compressed asphalt, insulating asphalt and asphaltic roofing paste, ought to be characterized by the following properties: they are elastic, do not soften at 40-50° C. or split or crack at low temperatures (—15a—20°). They contain bodies that volatilize with difficulty and do not oxidize at the ordinary temperature, and are therefore least exposed to decay through atmospheric influences. Pure bitumen is of a bright black color with a reddish shimmer and forms either a viscous, sticky, or else a hard and brittle mass which is not fluid under 35° C. It dissolves completely in carbon disulphide, oil of turpentine and chloroform, partly in petroleum spirit and benzol, and is almost insoluble in alcohol. By the name 'artificial asphalt,' or more correctly 'asphalt-surrogate' he designates those materials and products the chief component of which is not asphalt-bitumen, but coal tar pitch, petroleum pitch (according to him wrongly called

petroleum-asphalt or bitumen) or other similar resinous products, which cannot be discriminated outwardly from the natural products, but whose inferiority or uselessness shows itself in a short time because the binding substance does not possess the necessary physical and chemical properties."

Dr. Kovács accordingly limits the term "asphalt" to the genuine natural-asphalt, and will not hear of it being applied to the products of coal-tar or petroleum.

"Dr. Böhm also limits the term 'asphalt' exclusively to the natural product, but describes the residues remaining after the distillation of petroleum, lignite-tar, coal-tar, and fatty acids according to their degree of fluidity as 'pitch' or 'tar' with a prefix showing the origin of the product; as for instance, coal-tar, lignite-tar, petroleum-pitch, wool-fat-pitch, using 'bitumen' as a general term. Dr. Böhm agrees so far with Dr. Kovács that not only the artificial bitumen produced from coal-tar, but also that derived from petroleum, ought not to be described as 'asphalt.' He does not, however, say how petroleum-pitch may be distinguished physically or analytically from natural asphalt.

"Mr. Grittner informs me that he has not been able to make such a distinction, and I have also come to the same conclusion after the exhaustive series of experiments made with Mr. Krepelka which are described in the appendix.

"The tenor of Mr. Clifford Richardson's report amounts to the same. His argument is, that the formation of genuine, natural asphalt has been very similar to that of petroleum and that various transition stages exist between them, which easily explains why bitumen produced artificially from petroleum cannot be distinguished by any particular characteristic from natural asphalt.

"For the same reason and also on the basis of my own investigations I consider that the term 'asphalt' should also be applied to products made from petroleum, but that a distinction should be made between 'natural-asphalt' and 'petroleum-asphalt' (Erdöl asphalt). On the other hand, I quite agree that the products made from coal-tar (and lignite-tar) and pitch can be distinguished from the asphalts, not only in practical use, when they exhibit their inferiority, but also by laboratory tests, and should be classed as pitch and tar and not

as asphalt. I cannot, however, extend this prohibition to the products made from petroleum; firstly, because these products are genetically similar; secondly, because they cannot be distinguished from one another with any degree of certainty in the laboratory; and thirdly, because I have no positive proofs that petroleum-asphalt, in reference to its technical uses, cannot hold its own in competing with the numerous kinds of natural-asphalt. Above all, I should certainly say that the term 'natural asphalt' ought never to be used for the products artificially prepared from petroleum."

In the appendix is described in great detail, the researches that were conducted during six or eight months. Nine natural asphalts, four petroleum pitches and two coal-tar pitches were extracted with chloroform and the extract evaporated under a temperature of 150° C.

"The pure bitumen was then investigated regarding its specific gravity, melting point, the specific gravity of the chloroform solution, and its iodine value. Dr. Lunge then says, 'No experiments were made in the direction of fractional solution, fractional distillation, analysis by combustion, etc., etc., partly because only in a few cases had we sufficient material, and partly because the investigation of such a number of substances would have taken too long. As we learned from experience, a really useful classification of the various materials in this manner would have offered too many difficulties for technical as well as scientific purposes.'"

In his "Conclusions" he makes the following remarkable statements: "On the addition of petroleum benzine to a chloroform solution of coal-tar-pitch a precipitate is formed, which is not the case with natural or petroleum asphalts." It was not, however, found "possible to distinguish quantitatively between natural asphalt and 'petroleum asphalts' obtained from petroleum. This can scarcely be wondered at as it is a generally accepted view that the 'asphalts' (semi-solid or solid 'natural asphalt'), found in nature mixed with more or less mineral and other impurities, stand in very close relationship to the more or less liquid petroleum and are formed from these by analogous processes to those by which 'petroleum-asphalt is prepared artificially from oils.'"

The first paper by Dr. Köhler mentioned above starts out

by quoting the statement of Lieut. Malenkovic "that the ranging of petroleum pitches in line with natural asphalts can be proved scientifically only under constraint." His argument is, that in the formation of natural asphalts rapid processes have certainly not taken place, as is the case in the originating of the petroleum pitches under the influence of concentrated and fuming sulphuric acid. Against this must the objection be raised that at least here in America, and probably in other countries as well, large quantities of petroleum asphalt are traded in, from the process of formation of which the influence of sulphuric acid is excluded; they are simply residues of raw oil distillation, which frequently have been condensed (or polymerized) by blowing in of air or treatment with sulphuric acid. * * * In science the opinion prevails generally nowadays, that the natural asphalts are not only intimately analogous to the mineral oil, but that they should be considered straightway as having originated from them, whether a slow evaporation of the more volatile, with gradual oxygenation of the more complex ingredients is at the bottom of it as the older school holds, or that, which is more probable, a condensation and polymerization (Mabery and others), or finally, that besides these, simultaneously, a removal of hydrogen has taken place. (G. Kraemer). * * * This investigation has demonstrated that the action of sulphuric acid on raw mineral oil is even essentially polymerizing; resinous bodies possessing acid properties separating from the acid used in purification, after its dilution with water consist of polymerized petroleum components of a boiling point of more than 300° and are in no wise different from natural asphalt or bitumen. It makes no difference for the chemical nature of the asphalt, whether such process has been consummated slowly in the course of time or whether rapidly under the influence of chemical reagents, as this is a fact that holds good for other products of polymerization."

He then proceeds to compare ultimate analyses of natural bitumens and petroleum residuums and begs the whole question by asserting that the substances analyzed have not been proved to be different and are therefore identical.

He further strengthens his position by quoting the report

on the experimental work of Lunge and Krepelka which has been quoted at length in this paper.

I next take up the third paper under discussion that is mentioned above. After some personal explanation, Dr. Köhler says he selected certain analyses of asphalt for comparison, with the remark: "I have confined myself to stating the contents of hydrogen and carbon, not even mentioning the sulphur, which was advisable for the very reason that the analyses of the simultaneously adduced artificial asphalts (pitches) do not take the latter into consideration at all." He seems to be without knowledge of the fact that a large part, if not all of the sulphur has been burned out of the residuums in the process of distillation, and further contends in support of this remarkable statement, that "concerning the by far major part of the sulphur, however, it is not yet even settled whether it can be considered as chemically bound, because such proof, owing to the well known peculiarity of the sulphur to dissolve in high molecular carburetted hydrogen compounds is by no means an easy task."

Again he says: "It requires no argumentation to show that petroleum pitches, being the residues of distillation carried to considerably high temperatures, cannot contain any more fractions of low boiling point; why the mineral-pitches (Erdpeche) should furnish them is easily comprehensible, for they contain, just because they are not residues of distillation, a part of those highly volatile hydrocarbons of mineral oil out of which they originated by a process of polymerization or oxidation, which have remained excluded for some reason or other from transformation into asphalt. That those highly volatile fractions of the mineral-pitch are not to be considered as pyrogene products of decomposition of the former, is evident from the fact that it is possible to isolate them by extraction with suitable solvents, as well as by fractional distillation. Therefore no decisive significance can be attached to the distillation curve relative to the question as to the identity or difference of the natural asphalts and the petroleum pitches."

He then goes on to say: "In Mr. Richardson's opinion (See *The Mod. Asph. Pavement*, p. 145) the asphalts consist of a mixture of saturated and unsaturated polycyclic hydro-

carbons as well as derivatives thereof of sulphur and nitrogen. * * * True asphalts contain nearly no bitumen which is insoluble in cold carbon-tetra-chloride, but soluble in carbon-di-sulphide; the bitumen of the asphalts soluble in the last named solvents is called 'asphaltene' and cannot be melted without decomposition.

"The petrolenes or malthenes consist, according to the hardness of the bitumen, of 20 to 50 per cent of saturated di- or polycyclic hydrocarbons (polymethylenes) of the series of $C_n H_{2n-2}$ and $C_n H_{2n-4}$, the lowest member of which, $C_{13} H_{24}$, with a boiling point of $165^\circ C.$, has been found in Trinidad asphalt; they consist further of unsaturated hydrocarbons, which are easily soluble in concentrated sulphuric acid, the nature of which is not sufficiently understood; also of sulphur compounds which can be isolated in the same manner and have been found identical with those of the mineral oils of Ohio, Canada and California, and of nitrogen compounds which probably have the same relation to the polymethelenes as chinolin has to benzol.

"The asphaltenes are probably unsaturated hydrocarbons, or derivatives of them, in highly condensed form, possessing a very high molecular weight, but concerning their structure we know comparatively nothing. They contain the major part of the sulphur extant in asphalt (in what form is not said, K) and are characterized usually by the presence of remarkable quantities of it. The larger the content of sulphur the harder the asphalt.

"Normal asphalts leave, after heating, about 15 per cent coke residue, a fact which enables us to distinguish them by this characteristic alone from other solid bitumens."

I have made the foregoing extracts from these papers in order to present the views of their authors with sufficient clearness and thereby to set forth the grounds for the criticism that follows.

The President of the International Association for Testing Materials saw fit to appoint a committee consisting of a number of the most prominent investigators of bitumen then living. He placed at the head of the committee a very eminent man who had devoted many years to a totally different field of research. His report proves the absolute unfitness of

the selection. Had he possessed even an elementary knowledge of the subject submitted to the committee he would have pursued an entirely different course. He details, in his report, the apparent indifference of his associates, and then proceeds to demonstrate that the indifference was all his own, for the advice of the few eminent men who sought to coöperate with him was wholly ignored, and only inadequate and negative results of ill-timed and hasty investigations, in which his eminent colleagues took no part, were presented in this report, with an excuse that really effective research work was not entered upon for lack of time. Every member of the committee knew, as soon as he received the ambitious program circulated in three languages, that the chairman of the committee had no adequate conception of the magnitude of the task he had undertaken; hence, the seeming indifference to the importance of a subject in which every member of the committee would have manifested the liveliest interest had the matter been properly submitted for their active coöperation.

While this criticism may seem harsh, let us see if the report made by Dr. Lunge does not fully justify it. He says only two reports of any importance were received by him from any member of this committee; one from Dr. Kovács, the other from Dr. Böhm. They both emphatically declare that the term "asphalt" should not be used to designate artificial products, that is, residuums and pitches. Yet, ignoring the conclusions of these very eminent specialists in bitumen, he proceeds on purely negative evidence to assume that the term "asphalt" should be applied to substances made from petroleum, but not to those made from coal-tar and similar products.

His experiments were, first, the determination of the specific gravities of the extracted bitumens. Extracted bitumens are not technological products. An extracted bitumen may have a specific gravity identical with a petroleum residuum to the third place of decimals and yet contain elements, organic compounds, and even mineral ingredients, not found in the petroleum pitch. The extracted bitumens and residuums have a specific gravity of about 1.0; some sink in water and some float. If equal parts are dissolved in equal parts of chloroform or any other neutral liquid, no appreciable

difference in the specific gravity of the solutions could reasonably be expected.

Nor is the melting point of anything more than suggestive or of arbitrary value.

Perhaps more might be expected of the iodine values, but, when a proper consideration is had of the fact that solid bitumens are mixtures like liquid bitumens of proximate principles at present unknown in composition and proportional amount, such a purely empirical reaction as the iodine reaction signifies very little.

If any member of Dr. Lunge's committee had spent a summer's vacation with a graduate student investigating any of the vital problems involved in the manufacture of acids and alkalis, no one would more readily and accurately judge the inadequacy of any negative opinions they might express, than Dr. Lunge.

The work he left undone for lack of time, every asphalt chemist knows is the work that will fill the 20th century with honorable research by those who are so fortunately situated as to be able to conduct it. I can well remember the smile of incredulity with which Cyrus M. Warren listened to me, when in 1865 I opened several cans of California petroleum in his laboratory in Boston, and assured him that I had in them a new kind of petroleum that contained nitrogen and benzoles instead of paraffines. I well remember, too, the reluctance with which technologists admitted that California petroleum does not contain the hydrocarbons that are found in illuminating oil of good quality, yet this fact was demonstrated at an enormous cost, long before Mabery had proved by an elaborate research that those oils contain 20 per cent of nitrogenous basic oils, and little or no paraffines. Experiments without number, similar in many respects to those made by Dr. Lunge, in which I myself took part, had produced illuminating oils unsurpassed in color and appearance, some of which were pronounced by experts equal to any ever made, but they always proved inferior when burned under equal conditions with oils made from Pennsylvania petroleum.

Opinions, probabilities and negative results will never prove that unlike things are alike. Those who wish them

alike for commercial reasons can devote pages to fruitless argument and thousands of dollars of public funds to the attempt to make unlike things alike, but the truth always prevails in the end.

Dr. Köhler assumes that all natural asphalts are derived from petroleum. This assumption is not based on the observed facts of nature, technology or chemistry. He further assumes that the conversion of petroleum into asphaltum by natural causes is due to polymerization. When in California I proved by experiment that petroleums, placed in an open vessel on a window seat, exposed to direct sunlight, evaporated, both by weight and measure, with great rapidity, losing a portion of their contents that distilled at a temperature above the boiling point of water. I proved also by experiment in 1870, that California and Pennsylvania petroleums, subjected to parallel treatment, where air, ozone, chlorine, or other gas that would combine with hydrogen is aspirated through them, is in the first case converted into asphaltum-like compounds with loss of hydrogen, and in the second case is evaporated to a vaseline-like residue. While giving many negative results and possessing many physical properties in common, these petroleums are totally unlike. Any one can prove theoretically that paraffine molecules cannot be condensed by polymerization. If the molecule is doubled it is no longer a paraffine. Neither can complex molecules containing nitrogen and sulphur substitution compounds be polymerized, nor are they. The bitumens of Trinidad pitch give up sulphur as hydrogen sulphide below the boiling point of water, as I have proved by experiment. The California petroleums when put into a still yield large quantities of hydrogen sulphide at comparatively low temperatures. They cannot be distilled either with or without steam without decomposition. I have also proved by repeated experiments that both chloroform and turpentine solutions of Trinidad pitch and other natural solid bitumens are precipitated on addition of an excess of petroleum ether and these precipitates often contain sulphur. There is practically no sulphur in petroleum residuums. The original Dubb's process consists in treating the oil with sulphur, which escapes as hydrogen sulphide, burning out the hydrogen. Air passed through the hot oil burns

out the hydrogen in clouds of steam. When the crude distillates from these oils are treated with concentrated sulphuric acid the tanks are enveloped in stifling clouds of sulphurous oxide. There is every indication of very active decomposition of both oil and acid. To call all these phenomena polymerization and to liken them to the operations of nature is constraint that amounts to audacity. Where in nature are such reactions observed? As I have said elsewhere, we cannot reason from the processes of technology, bounded as they are by time and space, to the infinity of nature in which time enters without limit in sufficient quantity.

The statement of Malenkovic that Dr. Köhler quotes with emphatic disapproval, "that the proof for the chemical identity of petroleum pitches with natural asphalts has hitherto not been adduced any more than the proof that they are serviceable as natural asphalts," expresses an absolute truth, and is only met by Dr. Köhler with assumptions and probabilities. In his second paper on page 2 (of the paper) he gives two tables in which I am quoted as having published ultimate analyses of Trinidad pitch in which the sum of the percentages of carbon and hydrogen equal 100. I never made an ultimate determination of carbon and hydrogen in any solid bitumen in my life. I never had any time to waste in any such fruitless work. To quote such results along with those of Boussingault made more than 60 years ago, before the presence of sulphur in bitumen was suspected and when oxygen was determined by difference, is worse than a waste of time—it is folly.

After some rummaging, I found the source of this blunder in a paper that I published in the *Journal of the Society for Chemical Industry* for November, 1898. The sentence reads as follows: "Mr. Richardson gives a table by which he attempts to show that the bitumen of land pitch contains more carbon than the bitumen of lake pitch. His figures do not warrant his conclusion. His average of land pitch contains C83.68, H10.84, total 94.52 of hydrocarbon; of which 88.426 per cent is carbon and 11.574 per cent is hydrogen. His lake pitch contains C82.33, H10.69, total 93.02, of which 88.507 per cent is carbon and 11.493 per cent is hydrogen." If this blunder measures Dr. Köhler's familiarity with the literature

of bitumens, the vagaries of his conclusions need not occasion remark.

So Dr. Lunge refrains for lack of time in engaging in a research that Dr. Köhler regards as a by no means easy task, and both substitute for the laborious proof of the laboratory, those "scientific uses of the imagination" that appear as assumptions, opinions and probabilities upon which, as a foundation, any superstructure can be erected that suits the fancy. It is so easy to assume that natural fluid bitumens are not distillates because they contain very volatile constituents. Did Dr. Köhler ever study the coal-oil or Scotch shale industries? If he has, he has found the crude distillates of those shales and coals to very closely resemble natural petroleum of the Pennsylvania variety. They are both liquids that largely consist of paraffines, and neither of them, by nature or art, can be converted into asphaltum. It is only necessary to subject the coals and shales to distillation at the lowest possible temperature to obtain the whole range of paraffines found in Pennsylvania petroleum. If these crude distillates are again distilled, light and heavy fluids will be obtained, and residual pitches, that are black and lustrous with a conchoidal fracture and without either odor or taste; yet, they are neither anthracite coal on the one hand nor glance pitch on the other; they are simply, to use Mr. Richardson's felicitous phrase, "residual pitches."

This is the latest discussion on this subject. It is greatly to be regretted that Dr. Lunge's committee accomplished so little.

This discussion, however, deals with names as well as things. I am convinced that by a happy inspiration, Malo, in the first instance, formulated a title to his table of 1863 that cannot be improved, viz.: "*Tableau synoptique des matières bitumineuses.*"* Under this comprehensive title he arranged those substances that the scientific and technical knowledge of that period brought under it; but, the more than forty years that have since passed have greatly added both to our knowledge of the substances included by him in his table, and also to the number of substances properly in-

**Sur L'Asphalte*, M. Leon Malo, Paris, 1863.

cluded in such a table. This being the case, while the title may properly be retained as he used it, a rearrangement of the contents of the table becomes desirable.

Bituminous materials naturally fall into three great classes, viz.: Class A, pure bitumens, as they occur in nature; Class B, pyro-bitumens, or substance yielding by heat, educts and products more or less closely approximating natural bitumens; Class C, the artificial substances, resembling natural bitumens, obtained as educts or products from pyro-bitumens and other crude materials, usually by distillation, but often by chemical processes, which may properly be termed "factice" or "factitious bitumens."

Class A includes all of the natural bitumens, from natural combustible gas to the most pure and solid glance pitch, together with all the mixtures of bitumens with various kinds of minerals as they occur in nature.

These materials are:

(1) Natural combustible gas as it occurs in gas wells; also as it escapes from petroleum wells, and also as it escapes from springs of water, producing the phenomena of burning springs.

(2) Natural naphtha, usually nearly or quite colorless, and very volatile and ethereal, occurring in Persia and different parts of the world accompanying the water of springs, and in a few instances, flowing from wells with the escaping gas.

(3) Rock oil or petroleum, an oily fluid, varying in color from a pale amber through red and green to black. It occurs flowing from natural springs and accompanying water, also flowing from artesian wells and pumped from them. It is very widely distributed and at present forms the principal illuminating and lubricating material of commerce. The varying chemical composition of petroleum gives rise to a great variety of oils from different localities.

(4) Maltha or mineral tar. This material is a brown or black, intensely viscous, fluid. It has usually resulted from the evaporation and decomposition of petroleum. Only certain varieties of petroleum are susceptible to the necessary changes. Maltha generally contains gas and water entangled in its viscous mass, which causes the liquid when heated to

froth violently. Some of the water appears to be chemically combined with the maltha as water of hydration of basic oils that form a part of it.

(5) Fossil paraffine from Galicia, Utah and elsewhere.

(6) So-called asphaltic coals, Grahamite, Albertite, Gilsonite, etc., which yield paraffine on distillation.

(7) Asphaltum from the Dead Sea, Mexico, the West India Islands; glance pitch, yielding on distillation other hydrocarbons than paraffine.

(8) Maltha mixed with limestone or chalk, Seyssel, etc.

(9) Maltha mixed with sandstone, from many European and American localities.

(10) Maltha mixed with sand, Oklahoma, etc.

(11) Maltha mixed with earthy matter, Trinidad Lake, etc.

All of these pure bitumens may be refined at low temperatures or destructively distilled at high temperatures.

Class B includes all of the coals from peat to anthracite and all of the bituminous schists and shales. Anthracite is not strictly a pyro-bitumen, but it is introduced here to show its relations to other coals. This class of substances was very properly called by Dr. T. Sterry Hunt, "pyro-bitumens."

This class embraces:

(12) Peat, from localities all over the world.

(13) Lignite or brown coal, all over the world.

(14) Bituminous coal, all over the world.

(15) Semi-bituminous coal, all over the world.

(16) Anthracite coal, all over the world.

(17) Boghead mineral and other Scotch shales, with the paraffine shales of New South Wales, etc.

(18) Bituminous schists of Autun and other localities.

All of these pyroschists may be made to yield upon distillation, gaseous, liquid or solid, educts or products, resembling natural bitumens. The character of the distillate will depend upon the temperature. At low temperatures, the distillates will be dense and they will decrease in density as the temperature is raised until at very high temperatures the dissociation will be complete and the distillate will consist of hydrogen gas, with a residue of fixed carbon, "the carbon of the gas retorts," or coke.

Class C includes the educts obtained by distillation of pure bitumens and pyrobitumens at low temperatures; the products obtained from the same at high temperatures; and certain by-products of chemical processes. All of these products and by-products result from decomposition of either recent or fossil organic compounds by the application of heat or chemical reactions. It is often observed that liquid bitumens, such as the different varieties of petroleum, may be distilled into educts until a temperature is reached at which decomposition of the contents of the still follows, if the distillation proceeds. As an illustration: The so-called asphalt oils of southern California, when put into a still, yield at first, very volatile fluids that are colorless and ethereal. As the temperature rises, decomposition (dissociation) commences, hydrogen sulphide, and other gases, escape and may be trapped off from the condenser and used to heat the still. The liquid distillate increases in density, the odor becomes very rank, and the residue remaining in the still, when run out and cooled, is a solid mass, varying in composition and properties according to the proportion of distillate that has been run off, from a very brittle to a very cohesive and plastic solid, which is, as far as I could discover after a prolonged and very careful examination, asphalt only in name. These residuums are properly called "factice."

This class embraces:

- (19) Coal gas, street gas, illuminating gas.
- (20) Refined petroleum, illuminating oil, coal oil, kerosene.
- (21) Reduced oil, lubricating oil.
- (22) Paraffine, cosmoline, ceresine.
- (23) Coal tar, blast furnace tar, coke oven tar, yielding on distillation benzoles, dead oil, anthracene and pitch.
- (24) Residuum of petroleum, residuum oil.
- (25) Pittsburg flux, "Dubb's asphalt" bylerite.
- (26) Solid residuum of California and Texas petroleum.
- (27) Coke pitch and brittle residuums of petroleum, coal-tar pitch.
- (28) Coke from gas works and coke ovens.
- (29) Sludge acid tar and pitch.
- (30) Candle tar.

In these thirty items are included the bituminous materials known at the present time, many of which were unknown or but little known in 1863, when Malo first attempted to classify bituminous materials. I have made no attempt to give them specific names. I have simply enumerated in their proper order the substances to be named. I have too little familiarity with the French and German languages to even suggest names of these very varied substances, that may be uniform in the three languages. This was the problem submitted to Dr. Lunge's committee that was left unsolved. I suggest that no name or system of names should be applied alike to the natural and artificial substances found in classes A and C, with any expectation that present and prospective confusion will be avoided. To give a common name—asphalt—to the asphaltum of the Dead Sea, to Gilsonite, to Seyssel rock and the residuum of California petroleum, with other unlike things too numerous to mention, betrays a deplorable poverty of language; no more consistent with scientific accuracy than would be the calling of orthoclase, albite, labradorite, pumice, obsidian, glass and enamel by the name of feldspar.

From all that precedes the following conclusions are legitimate.

(1) That the proof is beyond question, that for years the interested vendors of bituminous products, especially those used in street paving, have been quibbling with the use of words until no confidence can be placed in their definitions.

(2) That numerous authorities have brought together convincing proof of the proper definition of the following English words:*

Asphalt, synonymous with Asphaltum; the solid form of natural bitumen.

Asphalte, a limestone saturated with bitumen, occurring at Seyssel and elsewhere. I have suggested the use of this word to designate not only limestone, but sandstone and sand saturated with bitumen, thus:

Asphalte, calcareous, Seyssel, Oklahoma, etc.

Asphalte, silicious, Lobsann, Oklahoma, etc.

*Report on Asphalt, Commissioners of Accounts of the City of New York, Feb. 3, 1904.

Asphalte, earthy, Trinidad.

Asphaltite, minerals occurring in true veins, having some of the properties of asphaltum and also of bituminous coal, yielding paraffine on distillation, Albertite, Grahamite, Uintaite, or Gilsonite.

Bitumen, a generic term including substances occurring in nature, in outflows or springs, and in veins, as natural inflammable gas, fluid petroleum, viscous maltha and solid asphaltum and asphaltite. It also occurs saturating and mixed with limestones, sandstones, sand or earthy matter. These mixtures are called asphalte. Bitumen varies greatly in physical properties and composition. It consists mainly of carbon and hydrogen with oxygen, sulphur and nitrogen in very complex compounds, regarding which chemists have much to learn.

Maltha, a viscous form of bitumen in many cases shading from petroleum on the one hand to asphaltum on the other.

Naphtha, a volatile ethereal form of bitumen, rarely met with in nature. A name frequently applied to the most volatile distillate of petroleum.

Natural Gas, combustible gas, escaping from fissures in the earth and springs (burning springs) and drilled wells. It often accompanies petroleum and escapes from petroleum wells.

Petroleum, Rock Oil, issuing from springs and wells. It is usually accompanied with water and "natural gas." Some kinds consist of a complex mixture of nearly pure compounds of carbon and hydrogen; others contain compounds of oxygen, sulphur and nitrogen.

(3) That the use of the word asphalt to designate bituminous rock leads to confusion and should be discouraged. That the use of the French word spelled with a final e to designate natural asphaltic mixtures whether calcareous, siliceous or earthy would lead at once to clearness of definition among English speaking people, but, perhaps is not equally clear in German and French.

(4) That the use of the words asphalt and bitumen to designate substances that are not found in nature is wholly unwarranted and cannot be justified by any plea of custom

when such custom leads to confusion in the definition and construction of specifications and other legal documents.

(5) That the adoption of specifications in which the word "asphalt" is defined in such a vague and unwarranted manner as practically to define nothing, admits of the use of a great variety of materials that are not natural products at all, nor are they asphalt at all, as defined by the highest authorities.

CHAPTER IV.
DERIVATION OF NATURAL SOLID BITUMENS.
(1) EVAPORATION.

While the most extensive deposits of solid asphaltum are found in injected veins that fill fissures in the earth's crust, the doctrine is advocated by numerous authors that petroleum is the primary source of all these solid bitumens and that these veins were originally filled with a liquid that has been inspissated. Inspissation when used in this connection can mean nothing else but evaporation. How the walls of these enormous crevices were held asunder while the inspissation proceeded; why the lower portions, often several hundred feet from the surface are not of a more liquid consistency than that at the surface; in what manner a residue of 10 per cent could fill the space occupied originally by the 100 per cent of liquid and what suspended the angular horses in a liquid at a point in the vein only a few feet below the cavities from which they fell, are questions that the advocates of this doctrine have never answered, although the questions were asked nearly forty years ago. The author has examined personally some of these veins and has read descriptions of others, and concludes that these questions are properly asked concerning every one of them and should be answered.

There are horizontal beds of asphaltum that occur in California, Mexico and Cuba and also in Albania and other localities in Europe-Asia, in the formation of which, evaporation of liquid bitumen as it oozed from orifices in rocks or was brought to the surface by the water of springs, has played an important part.

(2) DECOMPOSITION.

Whenever asphaltum has been formed from the evaporation of petroleum, the partial decomposition of the liquid bitumen has contributed to the successive changes that convert the petroleum into maltha, and continuing, finally result

in a solid bitumen, that, if unmixed with earthy matter or organic impurities, will, on being melted, produce glance pitch.

The paraffine petroleums will not produce asphaltum. These petroleums undergo evaporation and become a residue resembling solid paraffine more or less impure. Other petroleums, containing unsaturated hydrocarbons, less stable under atmospheric conditions than the paraffine, readily undergo both evaporation and decomposition. The California petroleums have both nitrogen and sulphur. Probably oxygen enters the compound, being substituted for both hydrogen and sulphur.

The conversion of fluid and semifluid bitumens into solid bitumens by burning out the hydrogen with sulphur, oxygen, ozone, chlorine, etc., has been repeatedly performed on both large and small scales in manufactories and laboratories. The results vary with the raw material selected. Paraffine petroleums, like those of Pennsylvania and Ohio, are mainly evaporated to a gummy mass resembling vaseline, being little acted on by oxidizing agents, while bitumens like those of California, consisting largely of unstable, unsaturated hydrocarbons, are readily acted on by them, and are converted into hydrogen sulphide, water or hydrogen chloride, which escape as a gas and a condensed body that is solid and resembles in many respects natural asphaltum. These factitious asphaltums will be treated further on in this work at greater length.

(3) POLYMERIZATION.

By polymerization is meant the aggregation or condensation of two or more molecules into a new molecule. As an illustration, two molecules of C_2H_2 may be condensed into one molecule of C_4H_4 , or three into C_6H_6 . As Prof. Mabery has remarked, polymerization cannot take place among molecules of the paraffine series as a multiple of any compound having the formula C_nH_{2n+2} would no longer preserve the ratio of carbon to hydrogen observed among the paraffines; but any compound of carbon and hydrogen having an equal number of atoms of carbon and hydrogen may be polymerized indefinitely.

Without any doubt, all three of these processes, viz.: evaporation, decomposition and polymerization, contribute to those changes which in nature convert liquid and semiliquid bitumens into solid asphaltum. It must not be assumed, that all solid bitumens are the product of these changes, for, it is inconceivable that the great fissure veins of asphaltum occurring in crevices in many localities could have been formed from petroleum which had filled these open fissures, for the long periods of time required to produce these changes. These bitumens occurring in fissure veins are the product of a natural distillation at a minimum temperature and pressure, from natural causes, acting upon deep-seated strata.

CHAPTER V. DERIVATION OF BITUMINOUS ROCKS.

There are several different varieties of bituminous rocks, which have without doubt been produced by phenomena, identical with or similar to those which have produced solid bitumens. They have resulted from the condensation of semi-fluid bitumens in the form of vapor in rock masses that were originally more or less porous.

It is not the condensation of petroleum, but maltha, that, penetrating these rock masses in the form of heavy vapors, has become condensed, thus forming a solid rock mass, sometimes completely saturated, and at other times presenting all degrees of partial saturation. The greatest variety of bituminous rock masses occur in Oklahoma. There are crystalline limestones presenting every degree of partial saturation; masses of magnesian chalk resembling the bituminous chalk of Neuf Chatel; carboniferous limestones consisting largely of fossil shells, every interstice of which is filled with bitumen. There are also sandstones saturated with bitumen and masses of sand and conglomerate that fall asunder as soon as the bitumen is removed. These rock masses and beds of sand were formed before they were penetrated by the bituminous vapors.

That the sand was not cemented into sandstone before the bituminous vapor penetrated it, is abundantly proved by the fact that when these bituminous sands are placed in boiling water, the sand and bitumen separate, the clean sand sinking to the bottom of the vessel while the bitumen rises to the surface of the water nearly free from sand. The bitumen thus separated is semi-fluid maltha, not petroleum.

A curious rock mass occurs in Oklahoma near Dougherty. It consists of fragments of limestone and chert cemented into a solid rock mass with bitumen.

When the bitumen is dissolved out of the Turrelltite of Texas, the mineral residue retains its form and is found to

consist wholly of shells and fragments of shells cemented together at their points of contact. That they had been subjected to the action of steam or hot water before they were penetrated by the vapors of bitumen is proved by the presence in the cavities of the larger shells of crystals of calcite in various forms along with fragments of shells. The carbonate of lime had been dissolved in the hot water, very likely under pressure, and redeposited in the cavities of the shells as calcite, before the bitumen was condensed in the interstitial spaces.

When the bitumen is dissolved out of the Seyssel rock there remains a coherent mass of nearly white chalk. These natural rock masses must have been penetrated by vapors that were distilled at the lowest possible temperature, hence the vapors were never subjected to overheating as is often the case with bitumens that are residues from destructive distillation, such as the residues from the various methods used in distilling petroleum. This fact accounts for the superior qualities often exhibited by these natural rocks over the most skillfully prepared artificial mixtures.

CHAPTER VI.

DERIVATION OF ARTIFICIAL SOLID BITUMENS.

Nearly forty years ago, the author discussed the chemical phenomena associated with the "distillation of bitumens" at high temperatures, technically termed "cracking." This term was at first used in the technology of liquid petroleum, and crude coal oil distillates, to designate the slow destructive distillation of residues that were too dense for illuminating oil and too light for lubricating oil, that accumulated in refineries. The process became of great technical value. No research has been undertaken, to the author's knowledge, to prove in what manner the products of cracking are related to the crude petroleum that is subjected to the process. Dr. C. F. Mabery has shown, on purely theoretical grounds, that paraffines cannot be molecularly subject to polymerization. On theoretical grounds it is equally certain that the paraffine molecule cannot be wholly cracked into molecules that are paraffines. Whenever a paraffine molecule is cracked, a part, at least, of the resulting molecules must be an unsaturated hydrocarbon molecule. For, cracking always results in a partial or complete dissociation of the carbon and hydrogen atoms. If the process is carried on at a low temperature the result is a fluid distilling at a lower temperature than the crude material, the molecule of which contains more hydrogen atoms in proportion to the carbon atoms, and a fluid that accumulates in the still that distills at a higher temperature than the crude material, the molecules of which contain less hydrogen atoms in proportion to the carbon atoms. If the oil is allowed to trickle into a white hot gas retort, free hydrogen will escape from the retort and the pure carbon of the gas retort will remain in it. If crude petroleum is cracked in a properly constructed still, a large percentage of the petroleum may be run out of the still of such a consistency that when cold it will appear as a solid mass, resembling a pure asphaltum in appearance. It is not, however, identical with natural asphalt.

tum, because in the processes of nature time enters in sufficient quantity, which may become practically infinity, while in the processes of technology the conditions of the problem compel comparative haste.

As a consequence, the products of the distillation of natural fluid bitumens, under ordinary atmospheric conditions, are almost without exception products of destructive distillation, or cracked products. Dr. Mabery has found that even the light, colorless paraffines cannot be distilled under atmospheric pressure without cracking. The colorless distillates from California petroleum cannot be distilled without cracking except under reduced pressure. In ordinary distillation on a large scale, California petroleum yields so much inflammable gas that it is trapped off from the condensers, and forms a large percentage of the fuel required to run the stills. The only source of this gas is the decomposition of the liquid bitumen, into a permanent gas that cannot be condensed, and residuum that becomes solid when cooled. Under these conditions, solid residues, resembling asphaltum are asphaltum or asphalt only in name, and therefore, in any nomenclature of bituminous substances should be given a distinguishing name, in order that they may not be confounded with natural solid bitumens.

There are also a number of other substances still further removed from identity with natural solid bitumens that are often, for various reasons, called asphalt or pitch. These are the solid residuums derived from the distillation of gas tar, coke oven tar, blast furnace tar, wood tar, etc. They are not identical with each other, and are in all respects very far removed from identity with natural solid bitumens.

Still another class of substances is obtained by the distillation of tarry by-products of various processes of chemical manufacture. Sludge acid pitch, candle tar pitch and the tarry residue of the wood pulp mills, are mentioned in illustration of this class of substances.

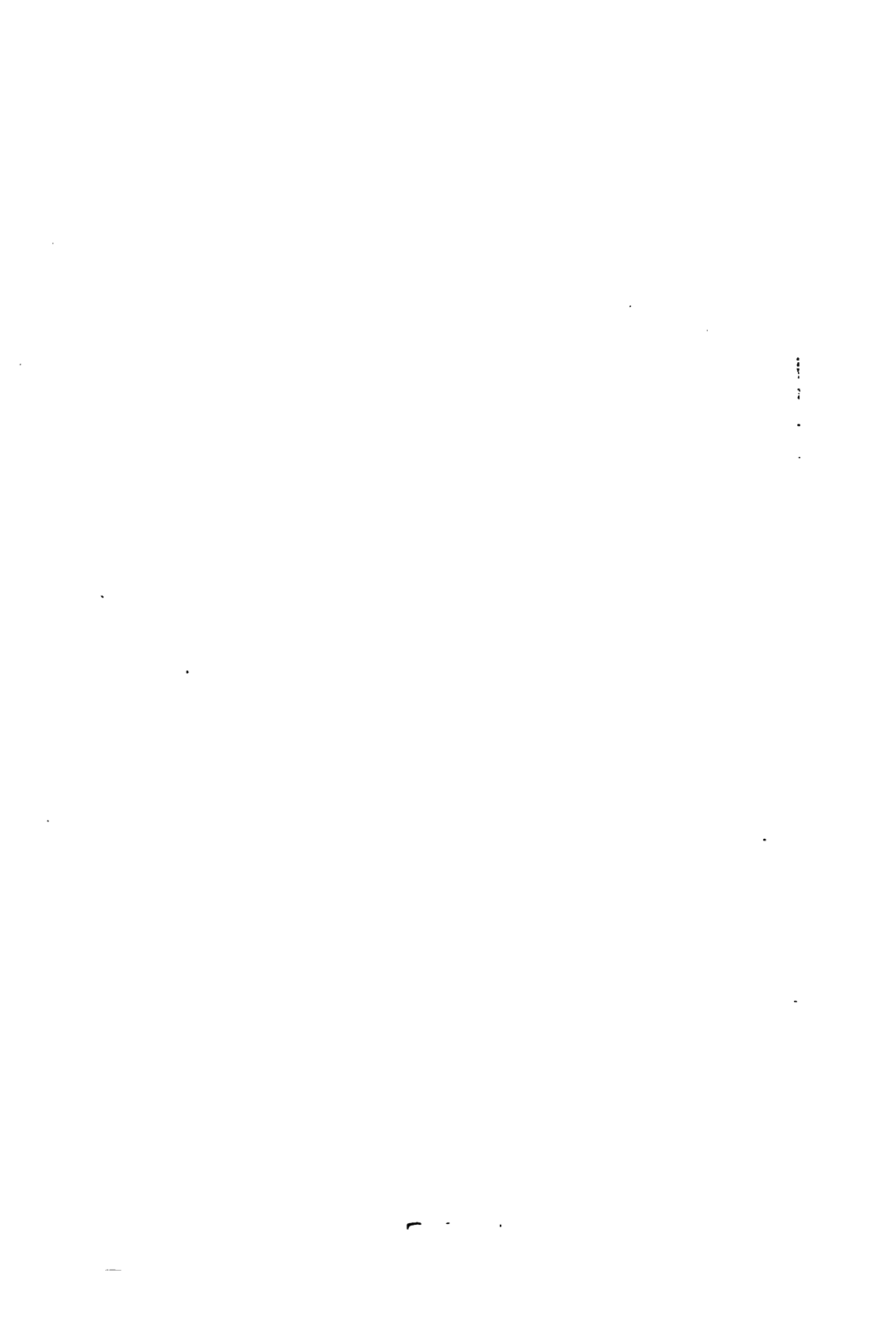
These highly artificial substances have been classed in our table of nomenclature as false or factitious bitumens, thus placing them in a certain relation to bitumen and at the same time separating them by a broad distinction from the natural bitumens that in some respects they simulate.

Dr. Jenő Kovács insists that "Holdé's proposal to classify asphalts and allied products into four groups, i. e., tar, pitch, asphalt and coke, according to their hardness, is not considered satisfactory to the asphalt expert as the origin of the material is not taken into account, whereas it is greatly to be desired that the name "asphalt" should in no case be applied to coal tar and naphtha products. Further, only three classes are held necessary, viz., tar, pitch and coke, as the pitch could be divided into hard and soft qualities if expedient."

"For the classification of tar, pitch and asphalt materials it is recommended:

"That the distillation products of coal tar and mineral oils be divided into three classes, viz., tar, pitch and coke. That the name 'asphalt' shall refer only to natural products, which occur only in the pure state or mixed with lime or sand, being, in the pure state, black and lustrous, and at the ordinary temperatures tough and sticky, or also solid and brittle, with a dropping point (see p. 274) not under 35° C.; easily and completely soluble in carbon disulphide, turpentine and chloroform, with difficulty soluble in petroleum spirit and benzine and almost entirely insoluble in alcohol."*

*Chem. Rev. Fett u. Harz-Ind., 1902, ix, p. 156-161; Jour. Soc. Chem. Ind., 1902, xxi, p. 1077.



PART II.
THE CHEMISTRY OF
BITUMENS.

CHAPTER VII.

GENERAL CONSIDERATIONS CONCERNING THE CHEMISTRY OF SOLID BITUMENS.

There are very few subjects of equal importance to chemistry and technology about which chemists know so little as the chemistry of solid bitumens. Much that passes for scientific statement respecting the chemical composition of solid bitumens reveals the paucity of our knowledge and also the fact that beyond a few ultimate elementary analyses almost nothing is known concerning the complex constituents of solid bitumens. Mr. Clifford Richardson has done a large amount of work upon the proximate principles that are found in the distillates from Trinidad pitch, but his conclusions appear to be assumed rather than proved. The author, by the use of solvents, has shown that Trinidad pitch is an exceedingly complex substance that cannot be distilled except destructively. The same may be said of every other natural solid bitumen that has been subjected to research by any method hitherto employed. Notwithstanding these admitted differences a great mass of facts, the results of various researches, conducted by many chemists over a long period of years, have accumulated and are on record as constituting the chemistry of solid bitumens.

The earliest research that was undertaken upon solid bitumens was that conducted by Boussingault in 1837, the direct results of which, though historically valuable, have been made in recent years to assume an importance out of all proportion to their intrinsic worth. In order that the readers may know for themselves exactly what Boussingault did, the author has translated and quoted his celebrated memoir entire, forming the subject matter of Chapter VIII.

CHAPTER VIII.

MEMOIR UPON THE COMPOSITION OF BITUMENS.*

Bitumens, so abundantly distributed upon the surface of the globe, and of which the uses appear to extend each day, have been little examined. It is to the deficiencies of chemistry that the confusion is to be attributed into which mineralogists have fallen when they have essayed to classify bitumens. One can correctly define the composition, and assign a place in the system to naphtha, idrialine, or mellite, but when glutinous bitumens are reached, the difficulty begins; one sees a liquid, ordinarily liquid, like petroleum, become viscous and present successively all degrees of consistency until asphalt, solid and brittle, is reached. It must be admitted, because of their great combustibility, that bitumens are essentially composed of carbon and hydrogen, and the water which some varieties yield on dry distillation, leads one to presume that they are not always free from oxygen.

My attention has just been directed to the bitumen from the mines of Bechelbronn, in the department of the Bas-Rhin. In this locality they exploit beds of bituminous sandstone, which are a part of a very extensive Tertiary formation. Important deposits of bitumen usually belong to recent epochs. They are also observed in basaltic tufas and trachytes, as at Pont-du-Château, in Auvergne. It is under equivalent geological conditions that the immense masses of mineral tar are encountered at Mendez upon the banks of the Rio Grande at the Magdalena.

When a bitumen is found in a fluid state, it suffices to separate it from the stones or impurities with which it is mixed. It is thus that the mineral tar can be obtained without much labor at Payta on the coast of Peru. But when the bitumen is intimately mixed with sand, as is the case in the Department of the Bas-Rhin, and at Seyssel on the banks of the Rhone, the extraction is made by boiling the mineral

*Translated from the French of J. B. Boussingault.

with water. The bitumen floats on the surface of the boiling water, and is removed by the aid of skimmers. The first skimmings contain some sand, and are submitted to a new boiling. The second skimmings, after being placed in wooden tubs, and left to drain, are heated in a large boiler until the water is all evaporated. While cooling, the fine sand which still adheres to the skimmings, is deposited. The bitumen thus purified is given to commerce.

Glutinous bitumens exhibit notable differences in their consistency according to locality. Those from Lobsann (Bas-Rhin) and from Seyssel (Ain) are tenacious at the ordinary temperature. When cooled, they become solid. These bitumens are properly tars, but they are especially employed in the manufacture of bituminous mastic. The deposits at Payta, those of the Magdalena, and of the Island of Trinidad, furnish bitumens that can be referred to the same variety.

There are no important deposits of asphalt known in Europe. Asphalt which one sees in the collections comes from the Dead Sea, or Lake Asphaltites. The uses of this mineral are excessively limited. I can mention one very abundant mine of asphalt; it is that of Coxitambo, near Cuenca, in Peru. Humboldt first described that locality, and admits that the asphalt is found in place in the superior part of the red sandstone.

I close this rapid review of the deposits of bitumen, by recalling that the outflows of naphtha and petroleum are met in abundance in the sandstone deposits of Asia, deposits that probably belong to a recent formation. The only fact which, in my opinion, indicates that bitumens are sometimes found in rocks of an ancient epoch, is that observed by Humboldt in Central America: This celebrated traveler saw petroleum springing from mica schist, beneath the sea at Punta de Araya, in the Gulf of Cariaco.

The bitumen of Bechelbronn, which constitutes the principal subject of my work, is viscous, and of a deep brown color. Its uses have given it the name of mineral grease, *steinöl*, Strasbourg grease. This material is substituted with advantage for greases of organic origin for lessening the friction of machines; and it is employed with success for greasing the axles of vehicles.

Alcohol at 40° acts upon the bitumen, especially with the aid of heat; it takes a yellow tint; after having been treated with alcohol, the bitumen becomes much more consistent. Sulphuric ether very easily dissolves bitumen; this solution permits the removal of the impurities that have escaped the refining.

Submitted to a temperature of 100° in a flask the bitumen of Bechelbronn yields no product. It is thus evident that it contains no naphtha. This conclusion must be admitted a priori, from reflection upon the treatment to which the bituminous sand has been subjected. As a consequence, I have determined whether the sand contained naphtha before its treatment. A quintal of the sand immediately after its extraction from the mines has been distilled with water and only a trace of naphtha has been obtained.

In raising the temperature by means of an oil bath to 230° , drops of an oily liquid are seen to pass. At that temperature distillation takes place with extreme slowness; but as one has in view the extraction of the volatile principles that bitumen could contain, without mixture of pyrogenous products, this degree of heat should be maintained; as, in order to obtain ten grammes of the oily matter distillation must be prolonged several days.

This volatile oily matter constitutes the liquid principle of glutinous bitumen, and as it forms the essential part of petroleum, I name it petrolene. In order to procure a sufficient quantity of petrolene, I have distilled with water the bitumen of Bechelbronn in an alembic which would hold two hectolitres of water in which I placed 12 to 15 pounds of bitumen.

The oil obtained by this means is very fluid, but it is sensibly colored brown. This was due to particles of the bitumen projected into the worm by the boiling water. The oil was rectified by distilling in a retort after drying over chloride of calcium. By this second distillation, the petrolene is obtained in a state of purity.

Petrolene is of a pale yellow; its taste is a little marked; its odor recalls that of bitumen. At the temperature of 21° the density is 0.891. A cold of 12° causes it to lose its fluidity; it stains paper after the manner of the essential oils; when it burns it pours out a thick smoke. Petrolene thickens at 280°

of the thermometer; alcohol dissolves a small quantity of it; it is much more soluble in ether.

The following analyses prove that petroleum is a hydrocarbon:

		Carbonic Acid.			Water.
I.	0.262 gave		0.837		0.303
II.	0.282 gave		0.896		0.311
III.	0.290 gave		0.927		0.310
IV.	0.289 gave		0.922		0.310
		I.	II.	III.	IV.
Carbon	0.833	0.880	0.885	0.884
Hydrogen	0.121	0.122	0.119	0.119
		<hr/>	<hr/>	<hr/>	<hr/>
		1.004	1.002	1.004	1.003

Petroleum is isomeric with essential oil of citron, essence of turpentine, and oil of copaiba. As I have not combined petroleum with sulphuric and hydrochloric acids, I have taken, in order to learn its atomic weight, the density of its vapor by the process of Dumas.

The vapor of petroleum weighs 9.415.

20 volumes vapor of carbon equals.....	8.432
16 volumes vapor of hydrogen equals.....	1.101
	9.533

Multiplying by 4, for the atomic weight:

80 atoms carbon, equal	3,060.8
64 atoms hydrogen equal	400.0
	3,460.8

After Dumas, the vapor density of essence of turpentine is 4.765. It is precisely half the vapor density of petroleum. Petroleum, like the oils that are isomeric with it, contains:*

Carbon	0.885
Hydrogen	0.115

After treatment with alcohol, the bitumen of Bechelbronn becomes stable; the alcohol becomes charged with petroleum, which it is easy to obtain, by submitting the alcoholic tincture to distillation. By the action of alcohol, it is impossible to remove all of the petroleum from the bitumen, as the bitumen in a measure loses its fluidity when the solvent

*Weight of flask full of air.....78.143 gms. Bar. 745 mm.
 Weight of flask full of vapor.....75.280 gms. Th. 21.2°
 Capacity of flask at 21°.....2.297 c. c. Pres. 728 mm.
 Air remaining in flask......20 c. c. Ther. 21.2°
 Temperature of vapor 310° mercurial thermometer.

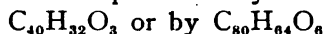
action of the alcohol diminishes. The distillation of the bitumen at a constant and sufficiently elevated heat, gives results no more satisfying. After different essays, the least that I have employed to deprive the bitumen of its volatile principle consists in an exposure to a temperature of about 250° in a Gay-Lussac's oil bath until there is no longer loss of weight. This method is prolonged; it is necessary to heat during 45 to 50 hours, even when operating upon a gramme of material.*

The solid principle of the bitumen which I obtained by this method is black, very brilliant; its fracture conchoidal; it is heavier than water. Toward 300° it becomes soft and plastic. It decomposes before it melts. It burns after the manner of resins, leaving a very abundant coke. When the fixed principle has been extracted from a bitumen, preferably purified by ether, it leaves no residue after its combustion. As this body possessed all the characteristics of asphalt, of which it forms moreover the essential part, I named it asphaltene.

0.299 of asphaltene burned with oxide of copper gave:

Carbonic Acid.	Water.	Carbon.	Hydrogen.	Oxygen.
0.814	0.268	0.750	0.099	0.148

This composition is represented by the formula:



which seems to indicate that asphaltene is the result of the oxidation of petroleue.

Asphaltene is insoluble in alcohol; ether, fatty oils, and essence of turpentine dissolve it. It is the same with petroleue.

The bitumen of Bechelbronn can be considered as a mixture of petroleue and asphaltene; that is at least a deduction from its analysis.

The bitumen analyzed had been purified by ether.

	Carbonic Acid.	Water.
I. 0.357 gave	1.125	0.360
II. 0.385 gave	1.211	0.400
	I.	II.
Carbon	0.871	0.870
Hydrogen	0.113	0.112
Oxygen	0.016	0.018

*By this method it is impossible to weigh the two principles of the bitumen; at that temperature a part of the petroleue becomes oxidized and passes to the solid state, or asphaltene.

This composition seems to prove that the bitumen of Bechelbronn contains:

Petrolene	0.854
Asphaltene	0.146

On that supposition, one should have:

Carbon	0.868
Hydrogen	0.112
Oxygen	0.020

Whilst I have not analyzed the bitumen of Lobsann, I have, however, proved that it contains the two principles that I have found in that of Bechelbronn.

In conclusion, it is seen that the glutinous bitumens may be considered as mixtures, probably in all proportions, of two principles, each of which has a definite composition. One of these principles (asphaltene) fixed and solid, approaches asphalt in its nature. The other (petrolene) liquid, oily and volatile, resembles in some of its properties, certain varieties of petroleum. It may, then, be conceived that whilst the consistency of bitumen varies, it may be said to infinity; it suffices that one or the other of the two principles dominates the mixture, thereby giving such or such a degree of fluidity.

A soft bitumen can always be converted to a harder variety by volatilizing by heat a portion of the liquid principles; it is thus that the Indians of Payta render fit for use in paying their vessels a bitumen naturally too fluid for that use.

The analogy that exists between asphaltene and the asphalt of the mineralogists leads me to ascertain if that analogy is sustained by its composition. As a consequence, I have submitted the asphalt of Coxitambo to analysis, which can be considered as a type of the species. The asphalt of Coxitambo has a largely conchoidal fracture; it is very smooth to the touch (il possède un grand éclat, on le prendrait); it is of a black color and is brilliant like obsidian. Its density is 1.68. The asphalt of Coxitambo dissolves with difficulty in petrolene and the fatty oils. With this difference only, which appears to prove the great cohesion of natural asphalt, the characters of the two substances are identical.

The asphalt of Coxitambo has been reduced to powder by means of a file. In two experiments I have found that its combustion left 0.016 of slightly ferruginous ash.

0.307 of asphalt (deduction made for ashes) gave upon analysis:

Carbonic Acid.	Water.	Carbon.	Hydrogen.	Oxygen.
0.819	0.261	0.750	0.095	0.155

This composition nearly approaches, as may be seen, that of the asphaltene extracted from the bitumen of Bechelbronn.*

*Ann. de Chem. et de Physique (2), lxiv, 141; Jour. Franklin Institute xxiv, 138; New Edinburgh Philos. Jour., xxii, 97.

CHAPTER IX.
THE USE OF THE WORDS PETROLENE,
ASPHALTENE, ETC.

This research of Boussingault was of great value at the time it was made, but modern methods have superseded those employed by him, and the investigation that he made in 1837 now possesses only historic value, were it not that the words petrolene and asphaltene, which he coined, and other words, have in recent years been introduced into the discussion of the chemistry of bitumen with new meanings, the value of which I shall further discuss.

The persistent use of the word retene, or retine, and more especially of the words petrolene and asphaltene, in current literature relating to solid bitumens and bituminous minerals, leads me to offer a protest against their further use, with reasons therefor somewhat in extenso.

The prominent position which Mr. Edward J. De Smedt has held in reference to asphalt paving in the United States has given his opinions great weight among those engaged in that industry. In 1893 he published in *Paving* a remarkable paper, which he said was designed "to open a discussion and investigation in regard to the required qualities of asphalt to form the best pavement." After making statements in reference to bitumens in general, he proceeded to make a few rather sweeping assertions, which may be carefully considered. He says: "Bitumens are generally composed of three different hydrocarbons: (1) retine, (2) petrolene, (3) asphaltene. The knowledge of these compounds is due to the important investigations of Le Bel and Muntz." "Retine—C, 78.84; H, 10.22; S, 10.78—is soluble in alcohol; submitted to heat, it gives off hydrogen sulphuret, marcaptan, and liquid hydrocarbon, and some coke is left. This compound is not desirable in asphalt.

"Petrolene—C, 80.60; H, 10.20; S, 9.20—is soluble in ether, and is the most important and desirable compound in

asphalt for paving purposes, since it is the compound which gives the viscous adhesive qualities to asphalt.

"Asphaltene—C, 78.00; H, 8.83; S, 12.89—is not soluble in alcohol or ether, but is soluble in chloroform and in bisulphide of carbon. It is this compound which gives hardness to asphalt, and the more asphaltene an asphalt contains, the more brittle and hard it is. So an excess of asphaltene is detrimental in asphalt employed for paving purposes."*

As the technical considerations involved in De Smedt's paper were met in a masterly manner by Captain Dolphus Torrey in a paper published in *Paving* in March, 1894, no further reference to that aspect of the subject will be made. De Smedt was very unfortunate in his manner of conducting the discussion, and it soon fell for want of cohesion.

When De Smedt's paper was published, I was in California and was not reading *Paving*. I was, however, soon brought in contact with the practical effects of this publication. As chemist to the Union Oil Co., of California, I was asked to determine the amount of retene in their products, and in correspondence I began to receive memoranda of determinations of retene. For many years the name retene had been applied to a crystallizable body soluble in alcohol which was derived from several varieties of fossil resin. As it is crystallizable, its formula had been carefully determined to be $C_{18}H_{18}$ or some other multiple of CH. A great number and variety of different compounds derived from it had also been analyzed. There has been no question about the composition and relations of retene for years as described in the general and periodical literature of chemistry. When I was asked to determine the amount of retene in an asphaltic residuum from California petroleum, and learned that a great many determinations of retene were being reported as made from asphaltum from many localities in different parts of the world, I began to wonder what had happened.

At last a prospective purchaser of California products requested us to ascertain the amount of objectionable retene contained in our material, and I set to work to make the determination. I had previously learned that methyl alcohol

**Paving and Municipal Engineering*, Nov., 1893, p. 206.

dissolves a certain percentage of our product, ethyl alcohol dissolves more, and amyl alcohol still more. By prolonged boiling in 95 per cent ethyl alcohol nearly as large a percentage was dissolved as in ethyl ether or petroleum ether. No crystallizable body could be obtained from any of these solutions, and I discovered that by varying the strength of the alcohols and the temperature at which they acted, the proportion of the residuum dissolved could be varied indefinitely. Further experiments upon crude California and other asphaltums gave similar results.

Later, I was asked by a friend, who was in correspondence with a chemist in regard to retene, or retine, I don't know which, if I had made any determinations of that constituent of asphalts. I related the facts as given above and suggested that the correspondent be asked, if he had obtained any crystallizable retene from any asphaltum, to tell how he did it. He replied that he had never determined retene, nor had he ever obtained a crystalline compound from any alcoholic solution of asphaltum. This experience confirms my own.

As to the word retine, I have made an exhaustive search of the dictionaries of several modern languages, as well as English, and can find only one word with that spelling. That is the French word which is equivalent to our word retina, as applied to the eye.

If I understand De Smedt, he refers to the researches of Le Bel and Muntz as his authority for what he says regarding retene, or retine. I have never seen any memoir, by either or both of these gentlemen, wherein any reference is made to any such substance, or in fact, to any alcoholic solution obtained from bitumen.

Captain Torrey has written quite in extenso upon the alcohol soluble from Trinidad pitch.* All that he has published upon the subject is to be found in Paving. He has very carefully conducted a large number and variety of experiments upon this alcohol soluble. He has discovered and recognized the differences produced by varying the strength and temperature of the alcohol, and he seeks to counteract

*Paving and Municipal Engineering, 1894.

their disturbing influence by what he calls a time limit. He allows the alcohol to act in exact periods of time, which he seems to think will give exact results. I do not think he can escape the relations of strength and temperature in any such manner, nor do I see any occasion for it, unless the petroleum ether soluble can be divided by using absolute alcohol at some fixed temperature. What is wanted is an absolute factor that can be repeatedly determined in the same specimen within reasonable limits; or, in language used by Dr. S. P. Sadtler, "What is wanted is a study of the action of a series of solvents of fixed purity upon different natural bitumens."*

One curious practical illustration of the use which has been made of this name is found in an "Asphalt Hand-Book," issued by the Standard Asphalt Co., of California. Dr. F. Salathé made an examination of their crude asphalt, and finding that acetone would dissolve more of it than petroleum ether, he made an acetone soluble and called it "petrolene (retenoid)." The portion insoluble in acetone he called "asphaltene (retine)." He further gives the "combined sulphur (chemically held in bitumens)" as 0.73 per cent. What meaning did Dr. Salathé attach to the word "retine" as used here? De Smedt's retine had 10.78 per cent of sulphur and his asphaltene has 12.89 per cent. Did he intend that these substances are practically identical? Moreover, De Smedt's petrolene has 9.20 per cent of sulphur; therefore, according to De Smedt, the California asphaltum should contain:

		Per cent.
Petrolene	67.50	Sulphur 6.21
Asphaltene	32.50	Sulphur 4.18
	<hr/>	<hr/>
	100.00	10.39

Dr. Salathé reports the content of sulphur to be 0.73 per cent. No more striking illustration can be found of the use of words that have no meaning.

So far as I am acquainted with the literature of asphaltum, it is not clear who first applied that name petrolene to that portion of asphaltum that may be soluble in ethyl ether or petroleum spirit. In the exhaustive work of Alfred H.

*Journal of the Franklin Institute, 149, 29.

Allen, upon "Commercial Organic Analysis" (Vol. II, page 374), published in 1886, mention is made of Boussingault's separation of asphaltum into "petrolene" and "asphaltene," but no further reference to the use of these names is made. It is possible that De Smedt first used that method of analysis and applied the names as they have since been used, but apparently we are indebted to Mr. Clifford Richardson for their use, with their present meaning.

Their use has proceeded of late years upon a totally erroneous conception of the constitution of asphaltic minerals and their relation to each other. If the arbitrary use of these names had been confined to Trinidad pitch, and the method or procedure of analysis of which they form a means of expression had been confined to the admitted determinations of the location of the spot upon the Island of Trinidad from which any given specimen came, less confusion would have arisen than has followed the attempt to designate many different things by one name. In a general way, it may be correctly said that there are no two asphaltums from different, widely-separated localities that are alike. If the same proportion to a 1/1000 of 1 per cent is soluble in any of the solvents of bitumen, it does not establish the identity of the two specimens. There has been nothing approaching the exactness demanded in chemical science observed in the use of the word petrolene. Ethyl ether, petroleum ether and acetone have all been used as it suited the convenience of the experimenter, and the percentage dissolved has been called petrolene, and various assertions have been made concerning petrolene and the relative value of asphaltums containing much or less of it; when at the same time the material dissolved from one asphaltum is one thing, and that dissolved from another asphaltum is quite another thing, and the different proportions of material dissolved from the same asphaltum by different menstrua are equally different. It is obvious that much that has been said in reference to petrolene applies with equal force to asphaltene. The names have been applied to various residues soluble and insoluble in various menstrua, and in various proportions. These residues possess various physical and chemical properties, and are in few respects identical. The name asphaltene has been used

to designate that portion of Trinidad pitch that is alone soluble in carbon disulphide. Mr. Richardson admitted, in his testimony given in the Peoria trial, that carbon disulphide did not dissolve the bitumen in Trinidad pitch within 1 per cent, and Wallace and Whinery, on the same occasion, described the material dissolved in this manner as an inert substance, without cohesion, and playing the same part in a paving cement as the same amount of sand.

I have found that if Trinidad pitch be first exhausted with petroleum ether and then with carbon disulphide, when the latter solution is evaporated there remains a brilliant black solid that cleaves from the vessel in thin scales. These scales are insoluble in petroleum ether, ethyl ether or alcohol, melted paraffine, and in fact most of the solvents of bitumen. They are wholly soluble in chloroform and benzole, and partially soluble in boiling spirits of turpentine, the portion insoluble appearing as a brown powder. If the scales are dissolved in benzole and petroleum ether added in large excess, a brown powder is precipitated that may be collected on a filter. When the powder is heated it becomes black and coheres. The portion soluble in spirits of turpentine may be wholly or partially precipitated, by an excess of petroleum ether, as a brown powder. When the solution of that portion soluble only in chloroform is evaporated and the residuum washed in ethyl alcohol, it appears as a brown powder without cohesion. These reactions show that the black scales obtained by the evaporation of the carbon disulphide solution above mentioned consist of a mixture of two, if not more, distinct substances. The first of these that is soluble in boiling spirits of turpentine is a very dense and exceedingly viscous fluid, possessing great tenacity, and it evidently plays a very important part in the cementing properties of Trinidad pitch. The portion that is only soluble in chloroform is a dark brown powder without cohesion, that does not melt when heated, but softens, becomes black, and at a red heat is decomposed, giving off a white vapor which takes fire and burns, leaving a carbonaceous residue that continues to burn at a red heat, leaving a small amount of ferruginous ash. It contained 5.87 per cent of sulphur.

The chloroform soluble is not a constant constituent of

asphaltum. Many asphaltums have not a trace of it; others have only a trace, while in others still, the percentage is very small. In those asphaltums in which the chloroform soluble is wanting, the percentage of turpentine soluble is often very small. There are no physical properties that serve to distinguish these asphaltums to the eye. The asphaltum that contains only a trace of chloroform soluble and but a small percentage of turpentine soluble may be in appearance a brilliant black, brittle solid, not to be distinguished by the eye from one that consists of from one-third to one-half of chloroform soluble. The relation of physical to chemical properties has not yet been determined.

It may be that the chloroform soluble represents, in some instances, that portion of the asphaltum that has been in some manner deprived of its hydrogen. This condition is not necessarily brought about by weathering, although it cannot be denied that weathered asphaltums almost invariably yield a comparatively large percentage of chloroform soluble. The following analysis of materials from the deposit at Trinidad furnishes a remarkable example of this fact. In the following table, No. 1 represents the average composition of the ten specimens of crude commercial lake and land pitch, analyzed by Miss Laura A. Linton. No. 2 is the average composition of two specimens of alteration products of Trinidad pitch, one of which came from the lake, and the other from outside of it. I have also similar material from the weathered portions of asphalt veins in California.

	No. 1.	No. 2.
	Per cent.	Per cent
Petroleum ether soluble	34.612	20.306
Turpentine soluble	12.375	17.843
Chloroform soluble	5.757	13.968
	<hr/>	<hr/>
Total bitumen	52.744	38.981
Organic material not bitumen	11.098	9.706
Mineral matter	36.160	38.175
	<hr/>	<hr/>
Total bitumen soluble in petroleum ether	65.660	38.981
Total bitumen soluble in turpentine.....	23.391	34.195
Total bitumen soluble in chloroform.....	10.925	26.824

The material of which the analysis is given in column No. 2 may be what Mr. Richardson has called "chocolate

pitch.”* It is a light brown, pulverulent solid, in form somewhat columnar, like starch, and just as easily rubbed into a powder between the fingers. It contains nearly three times the percentage of chloroform soluble that occurs in the average commercial pitch. Somewhere between the chloroform soluble of 10.925 per cent, which is found in the average commercial pitch, and the 26.824 per cent found in this alteration product, the Trinidad pitch loses its tenacity and becomes friable. Of course, as the chloroform soluble is increased, it must be at the expense of the other ingredients. The petroleum ether soluble in this case is only about one-half the proportion given in colume No. 1, the ratio being 38.981:65.66. The ratio of the chloroform soluble to the total bitumen is, in No. 1, 1:9.163, and No. 2, 1:2.789. The investigation of these problems has only just been entered upon, but it is a research of vast importance, and must in time command attention.

When these figures were first developed, from the results of Miss Linton's analytical work, it was hoped that some satisfactory explanation of the peculiar properties of glance pitch might be deduced. The claim that glance pitch is geologically old pitch is found to be entirely erroneous. The following figures show the compositions of five pitches, all of which are supposed to be Cretaceous or older:

Per cent of petroleum ether soluble in total bitumen....	{	No. 1, 25.4605
		“ 2, 35.0870
		“ 3, 38.0300
		“ 4, 49.9590
		“ 5, 51.0430
		“ 6, 8.5106

Nos. 2, 5 and 6 are very brilliant glance pitch; the others are equally hard, but not as brilliant. The chloroform soluble varies in these from less than 1 per cent in No. 6 to 32.5 per cent in No. 4. Just as brilliant and hard glance pitch as any of these, I know to be a melted tertiary asphaltum, of which more than 75 per cent is soluble in petroleum ether. Such discordant results, obtained from such a large number of asphaltums from widely different localities, have confirmed the opinion that the peculiar properties of glance pitch do not

*See Clifford Richardson, *Journal Soc. of Chem. Ind.*, xvii, 14.

depend upon chemical composition, but are the result of the melting of the asphaltum.

The term "glance pitch," is therefore, no less to be discarded. While retene or retine are terms for which no *raison d'être* can be discovered, petrolene, asphaltene and glance pitch, are terms that once had meanings which are now outgrown. The use of all these terms should therefore be omitted and avoided.

In the article published in the March number of *Paving* for 1894, Captain Torrey says, in reference to the use of the names retene, petrolene and asphaltene: "With the present knowledge of them, it would be better not to use these misleading names, but others more appropriate." In this opinion I fully agree, and would add that for some time past I have sought to discard them, and to report the percentage soluble in petroleum ether and other solvents as "the petroleum ether soluble," and not as petrolene, etc. For these reasons these terms will not be further used or discussed in this work.

CHAPTER X.

THE ULTIMATE ANALYSIS OF SOLID BITUMENS.

Solid bitumens consist of a great variety of mixtures of complex compounds of carbon and hydrogen together with compounds of carbon and hydrogen with oxygen, sulphur and nitrogen. Nearly or quite all natural solid bitumens contain organic salts of iron and alumina resembling the organic salts of alumina found in amber and coal.

The ultimate analysis of such an exceedingly complex mixture of substances presents some difficulties.

The carbon and hydrogen may be determined with Warren's apparatus for combustion in oxygen gas, using proper precautions with reference to the sulphur present, or any other of the ordinary processes for elementary analysis. This is a well tried method the value of which has been thoroughly tested by Mabery and others. I have repeatedly obtained results by its use that left nothing to be desired.*

Recently Porter R. Shimer has described a method for determining carbon and hydrogen in a platinum crucible.†

Oxygen is usually determined as a residual difference—a method of determination, open to grave criticism. For many years I have doubted the existence of oxygen in either natural or artificial hydrocarbon nuclei, that are constituents of solid bitumens. So far as my observation has gone, both in the field and in the laboratory, atmospheric oxygen, especially when dissolved in rain water as a natural phenomenon, or oxygen, when made to react with bituminous materials in the laboratory, does not enter the hydrocarbon nucleus by substitution for hydrogen, but subtracts hydrogen from the nucleus, forming water which escapes, leaving a condensed molecule which contains proportionately more carbon and

*The original description of Warren's apparatus was published in 1864 and 1866 in the *Memoirs of the American Acad. Science*, Boston, the *American Journal of Science* and the *London Chemical News*.

†Porter R. Shimer, *Jour. Am. Chem. Soc.*, xxi, 557; xxv, 237, 997.

less hydrogen, remaining a hydrocarbon and not an oxyhydrocarbon.

Sulphur has been recognized as a constituent of bitumens for many years. In the anonymous abridged translation of Boerhaave's Elements of Chemistry, published in London in 1732, p. 18, before referred to, under the head of sulphurs, are described "Brimstone, orpiment, petroleum, naphtha, asphaltum, Jewish pitch, pissasphaltum, jet, litbrantbrax, amber and oil of earth." Judging from the detailed description, some of these substances are products of the imagination, but the classification shows that certain similarities were early recognized.

Those who have analyzed bitumens without proper attention to the presence of sulphur, have until recently attributed to the presence of oxygen a residual difference that should properly have been credited wholly or in part to sulphur. Again, after the presence of sulphur as an almost constant constituent of natural solid bitumens had been admitted, a number of determinations of sulphur have been published that have been made by methods not always reliable, the results of which have led to some confusion and to statements concerning the sulphur content of bitumens that appear to me somewhat exaggerated. In illustration it has been stated that some solid natural bitumens contain 10 per cent or more of sulphur, when it is easily demonstrated that one part of sulphur melted into nine parts of a bitumen free from sulphur, produces a substance wholly unlike any natural bitumen. Nevertheless, without doubt sulphur has played a very important part in the formation of many solid bitumens, that are in many instances largely the result of the action of sulphur upon fluid or semi-fluid bitumens. Sulphur burns out the hydrogen from bitumens, and this reaction may proceed slowly at ordinary temperatures or rapidly at higher temperatures. It is not necessary that the sulphur should be free. It has long been known that sulphates are deoxidized when brought in contact in solution with dead organic matter. If the organic matter has already been distilled into bitumen, the reaction proceeds through double decomposition, a carbonate of the base being formed and hydrogen sulphide, free sulphur, and a sulphur substitution compound remaining as

a part of the bitumen.* In proof of this latter statement we have the direct evidence furnished by Mabery's researches upon Lima petroleum. This is a paraffine petroleum, and the sulphur compounds isolated are paraffine derivatives. As almost nothing has been proved concerning the sulphur compounds of solid bitumens, there is very little upon which to base any general conclusions concerning them. The sulphur content of solid bitumens is at present an open question.

C. M. Warren in March, 1865, published in the Proc. Am. Acad. Sciences a paper "On a New Process for the Determination of Sulphur in Organic Compounds, by Combustion with Oxygen Gas and Peroxide of Lead."†

Of the merits of the process I have no practical experience.

Until recent years few, if any, investigators who have written upon this subject have a word to say concerning the method that they used for determining the sulphur; consequently I have never had any other instructor than experience. This experience began several years ago while in southern California, in an attempt to establish, at the request of the Patent Office examiners, specific differences between a solid asphaltic residuum obtained from California petroleum, the same oxidized by prolonged action of air, and also by treatment with sulphur. Nearly all of this work was carried on in association with Dr. Frederick Salathé, who said he had examined a large number of natural and artificial bitumens for sulphur. The residuum and sulphurized residuum were tested for sulphur by boiling with fuming nitric acid in a flask with an inverted condenser, and no sulphuric acid was found in the liquids. This method of testing was not then further investigated. Other reactions showed that a compound was formed, which, when oxidized with nitric acid, produced styphnic acid, which is a trioxynitrobenzol—a compound not only interesting, as showing the action of the sulphur, but also as showing that the residuum consisted of benzols. Neither transmitted air nor direct oxidation with nitric acid converted any portion of the sulphurized residuum into styphnic acid. Treatment of

*Geolog. and Chem. Essays, T. S. Hunt; pp. 87, 99, 145, 163 and 230. S. F. & H. E. Peckham, Jour. Soc. Chem. Ind., Dec., 1897.

†Am. Jour. Science, xii, Jan., 1866.

the residuums by deflagration with Na_2CO_3 and KNO_3 showed sulphur in the residuum, but only a trace in the same after treatment with sulphur at a temperature of 400°F . At that temperature the sulphur almost fully burned out with hydrogen, and the bitumen was left dryer and more brittle. Later, I had occasion to determine the sulphur in various bitumens, and recourse was had to boiling with fuming nitric acid, with an inverted condenser. After repeated attempts it was discovered that no quantitative determinations of any value could be made in this way. Addition of potassium nitrate, chlorate, or permanganate was of no avail, and I finally abandoned all attempts in this direction. I believe I have tried every method for the determination of sulphur except the bromine method, and that has never appeared to be practicable with solids. Nor has the method of Carius, which I mention here, for fear that by its omission I might be misunderstood. The method which I finally adopted, is one that was used for the determination of sulphur in the Pacific Coast coals. (See *Geology of California*, vol. II., *The Coast Ranges*, App., Cambridge, Mass., 1882, p. 45.) It is susceptible of great accuracy if conducted with care. Two gms. of the bitumen are intimately mixed in a mortar with 16 gms. each of pure, dry Na_2CO_3 and KNO_3 and the whole projected in small portions at a time into a 2-oz. platinum crucible, heated to dull redness, or no hotter than is necessary to cause the mass to deflagrate. Experience will soon teach the manipulator how best to conduct the operation. After deflagration and complete fusion, the mass is dissolved in water, hydrochloric acid added, and the solution either evaporated for removal of silica or immediately filtered, and the sulphuric acid precipitated in the hot acid solution. The barium sulphate is washed, dried and weighed with the usual precaution.

I repeat that this method is susceptible of great accuracy if conducted with care, and it has the advantage of bringing into solution all of the mineral matter contained in the bitumen.

It was, however, criticized by E. H. Hodgson in the *Journal Am. Chem. Soc.*, November, 1898, in a paper in which the results obtained by several methods used upon the same materials were compared. In the *Jour. Am. Chem. Soc.* for

September, 1899, S. F. and H. E. Peckham replied to the criticism of Mr. Hodgson as follows:

The paper is evidently intended to be a description of a fair comparative test of the value of the several methods used for the determination of sulphur in the different varieties of bitumen examined.

We wish to call attention to a number of unrecognized, or at any rate, unmentioned conditions, which, in our opinion, render the results, given by Mr. Hodgson, variable, and to some extent unreliable.

Of the specimens selected for analysis, it is to be said, that the two specimens called "Trinidad Lake" and "Trinidad Lake refined" are very peculiar substances. They, in common with all other Trinidad pitch, consist of a mixture of bitumen, mineral matter, organic matter that is not bitumen, and a considerable proportion of ferric and aluminic oxides, that are combined with organic radicals to form complex salts. There are sound reasons for believing that some of the sulphur is free, some of it in combination with iron as pyrites, in an extremely minute state of division, and some of it in combination as thio-salts, in which it performs a linking rather than saturating function.

There can be no question that the action of nitric acid on this complex mixture of various substances results in the formation, not only of sulphuric oxide, but of other oxides, of alumina and iron, that will almost certainly form double barium salts with sulphuric acid, that are nearly or quite as insoluble as pure barium sulphate, and consequently follow, or accompany the barium sulphate, even to the final weighing.

The specimen denominated "Trinidad crude" and further described as "crude asphalt from Hadley's diggings, about one mile from Trinidad Lake; it is known as 'iron pitch,' being the hardest asphalt found in Trinidad," is not asphalt at all, but is a residue from the natural distillation of the pitch by jungle fires, found in small masses, and in small quantity, all over the deposit, both within and without the lake, and it is uniformly rejected as rubbish. It has been subjected to such a temperature that all of the water has been expelled, and the whole mass melted and brought to a condition of semifluidity. Apparently the sulphur is in part expelled, and

that which remains is evidently brought into such a condition that the nitric acid process fails to produce the reaction essential to the formation of double salts, as the results of the analyses by the four processes used by Mr. Hodgson are essentially alike. The results obtained from Cuban, Alcatraz, and California asphaltum are evidently subject to the same criticism as the Lake pitches, in a less degree.

The deflagration method, as described in Mr. Hodgson's paper, is not the method used by the authors. We never used a porcelain crucible; first, for reason of its form, and second, for reason that the fluxes used will react with the porcelain, making it impossible to determine the iron, alumina, and silica in the assay.

We have modified to a slight degree our method of procedure, as experience has suggested, until finally we have weighed out such an amount of the assay as will represent about 0.5 gram of bitumen. This is very thoroughly mixed with 15 grams each of pure dry sodium carbonate and potassium nitrate. The salts are first thoroughly pulverized and mixed in an unglazed porcelain mortar. Two-thirds of the mixture are then removed to a sheet of glazed paper. The assay is mixed in the mortar with the flux in the most thorough manner and then removed to a second sheet of glazed paper. The mortar is carefully rinsed with the remaining flux in two successive portions. The whole of the flux and assay are brought to a uniform mixture on the glazed paper. The mixture is then brought, small portions at a time, into a 2-ounce platinum crucible, heated to dull redness. No fusion with a blast-lamp is necessary, as the assay is in quiet fusion when the last portion has deflagrated. A large excess of flux lessens the violence of the combustion and also lessens the liability to loss by spattering.

The contents of the crucible are then dissolved by allowing it to remain covered with water in a beaker, preferably over night. When the solution is complete, the crucible is washed off and the contents of the beaker rendered acid with hydrochloric acid. The solution is evaporated to dryness over a water-bath, the silica dehydrated, moistened with hydrochloric acid, treated with water and the silica filtered off, ignited, and weighed. The solution is rendered alkaline with

ammonia, boiled until the excess of ammonia is removed, and the precipitate of iron and alumina dried and weighed as usual. The iron may be found in another portion with potassium permanganate and the alumina determined by difference. Lime may be determined as oxalate if desired.

The solution, freed from silica, iron, alumina, and lime, is brought to a boil, acidulated with hydrochloric acid, and the sulphuric acid precipitated with barium chloride, added in small portions at a time from a pipette. This method for the determination of sulphur is susceptible of great accuracy, if conducted with care. It requires great care from the beginning to the end. Mr. Hodgson's results do not indicate great care,—they are not sufficiently concordant.

We have not found the slightest difficulty in bringing out concordant results to the second place of decimals, and sometimes to the third. The method has also been proved presumably correct by reason of determinations made by first estimating the sulphur in a very pure asphalt and then in the same asphalt to which a weighed quantity of pure, dry sulphur had been added. The results showed the amount of sulphur in the pure bitumen plus the amount of pure sulphur added.

It is to be noted that in materials exceptionally low in sulphur, it is necessary to take a larger portion than is usually found advisable in the use of this process, and when so much of the asphalt is burned it becomes absolutely necessary to use a larger proportion of the flux, otherwise some of the assay will escape oxidation.

It has not yet been shown that mercaptans and similar sulphur compounds exist as constituents of crude bitumens in such amount as to be worthy of consideration in this connection. This method is not recommended as superior to the method of Carius in ultimate research, but is recommended for the determination of sulphur in solid and semisolid bitumens for technical purposes, as very much simpler and more rapidly executed.

As the next step in the evolution of a reliable process for the determination of sulphur in solid bitumens we have in the *Jour. Am. Chem. Soc.* for September, 1905, p. 1188, a paper on an "Inner Crucible Method for Determining Sulphur and

Halogens in Organic Substances," by S. S. Sadtler. The author states:

"To all workers in organic chemistry who have to make determinations of sulphur and halogens in research or commercial work, the use of the Carius furnace is almost always found to be troublesome. It has always been so to the writer, and after many plans to avoid its use, he devised the way here described.

"The general idea does not seem to be a new one, as Dr. Edgar F. Smith said in discussion upon an unpublished paper read by the writer before the Philadelphia section of this society, that he had used an inverted inner crucible with caustic lime as a reagent to determine chlorine in organic substances when a student. More recently Shimer* described an inner crucible method for determining carbon in steel, etc. The writer tried inverting small platinum and porcelain crucibles in large platinum crucibles, but with sulphur compounds containing volatile constituents the oil not only began to distill before the absorbing layer of the reagent became sufficiently heated to take up the sulphur, but also came off too fast.

"Successful results even with fairly volatile oils containing sulphur were finally obtained by modifying the inner crucibles so as to meet the requirements. It was made at first of sections of glass combustion tubing, the idea being to keep the charge to be analyzed as far as possible from the points of application of the heat, and to have a relatively poor conductor of heat, which was readily obtained with glass. The charge was put in the rounded end, which had been drawn out to seal it and packed with Eschka mixture. This made a fairly satisfactory apparatus, for, while the absorbing mixture became red hot, the oil was only gradually vaporized. It was found, however, that the glass was acted upon by the alkaline mixture and sulphur seemed to be taken up at times in an adhering mass in one determination and given off in another. An ordinary 20-gram platinum crucible was used for the outer crucible. The inner crucible of glass, however, was not considered practicable and a cylinder of platinum closed at the upper end was tried, and it was found that the Eschka mixture expanded with heat and lifted the cylinder.

*Chem. Eng., November, 1904.

The following apparatus was, therefore, tried after other intermediate attempts, and found to be satisfactory.

"The outer crucible is made with straight sides like an inverted truncated cone with a tightly fitting lid. In the bottom is a cylindrically shaped indentation so as to extend the highly heated zone into the inner crucible.

"The inner crucible was made with sides very nearly parallel to the outer crucible when inverted within it. Small rings of platinum were soldered to the wide, closed end, so as to keep it centered with respect to the outer one.

"The open end is made as thin as possible so as to minimize the tendency to conduct heat. The edge fits about midway between the walls of the central indentation and the outer crucible.

"The method of procedure varies somewhat with the material for analysis. With solids, careful insulation of the two crucibles is not necessary. With liquids, especially those containing sulphur, careful insulation is requisite, and with very volatile ones, such as carbon disulphide, it is necessary to fill them into small capillary bulbs such as are used for sealed tube combustions.

"An important difficulty in the way of getting accurate results with this method was the puffing of the Eschka mixture, and the author found that the chemically pure light magnesia he was using contains 12 per cent of water, and when this was driven off, and carefully dried, sodium carbonate was used, that lifting the crucible and puffing ceased. The mixture was made up of equal weights of dried magnesia and sodium carbonate instead of 2 to 1.

"The substance is first weighed into the inner crucible, which is placed open end up on the balance pan. It is found desirable to take the minimum weights which will give final precipitates suitable for weighing. Thus about 1 gram of sulphur compound containing 1 per cent sulphur is taken.

"An amount of a halogen compound containing 1/20 gram of actual halogen, depending somewhat upon the one in question, and about the same amount of phosphorus containing substance.

"Enough mixture is then put in to absorb the substance, when it is a liquid, and then filled nearly to the top with mod-

erate tamping. Plain ignited magnesia is then put in level with the top, so as to keep the soda away from the platinum, as the platinum on the bottom of the crucible is attacked by the hydrate of soda which is formed at the high temperatures, or by some compound with reducing gases.

"Freshly ignited white asbestos is then put around the raised portion of the bottom of the outer crucible to keep the two crucibles from being in actual contact. It is then lowered over the inner crucible and the two crucibles inverted. A layer of magnesia mixture about $\frac{1}{4}$ inch deep is then put in between the crucibles. The outer crucible is then put through a hole in a piece of thin but fine asbestos board so that very little, if any, of the sides can be exposed to the direct action of the flame.

"A very small pointed flame of a Bunsen burner is now used so that the flame is chiefly in the indentation on the bottom. If gases do not come off from the crucible in three to five minutes with this flame, the heat is increased, and when no more odor is noticeable the crucible is placed in a piece of asbestos having a larger hole, so that half the crucible may become red hot and is kept so for ten minutes. The flame is then withdrawn, and when cool the inner crucible is carefully raised and tapped, so that its contents are dropped into the outer one, when the carbon is burned out with a shield of asbestos to protect the contents from the sulphur gases of the flame in the case of sulphur determinations.

"For sulphur determinations the contents of the crucible are washed into a beaker. Bromine is added to oxidize sulphites, etc., the solution is filtered, acidified and precipitated with barium chloride, as in the case of determinations of sulphur in coal.

"With halogen compounds the contents are washed into a beaker and dissolved with pure nitric acid, the asbestos filtered off and the halogen precipitated by means of silver nitrate. The chief precaution the author (S. S. Sadtler) has found necessary is to bring all the contents of the charge to a red heat to break up any oxygen compounds of chlorine.

"This method applies to all organic combustions of sulphur, the halogens and phosphorus, but the amount taken

must be limited to take only a moderate final weight of barium sulphate or silver halide, such as 0.1000 to 0.2500

The Determination of Sulphur in Petroleum and Bituminous Minerals, by F. C. Garrett, D. Sc., and E. L. Lomax, B. Sc.,* is as follows:

"Many methods for the estimation of sulphur in bituminous minerals have been suggested, but Hodgson† has shown that none could be trusted except that of Carius, and this method, though accurate, is very tedious. We have found that, by some modification in the details, the familiar method of heating with a mixture of sodium carbonate and lime or magnesia can be used even in the analysis of petroleum. A convenient quantity (i. e. from 0.7 to 1.5 gm.) of the substance is placed in a small platinum crucible, intimately mixed with 3 or 4 gms. of a mixture of four parts of pure lime to one of anhydrous sodium carbonate, and the crucible completely filled with the lime-soda mixture. A larger platinum crucible is placed over the small one (mouth downward), the whole inverted, and the space between the two crucibles filled with the lime-soda mixture. The mouth of the crucible is covered with a thick pad of asbestos board, and the apparatus placed in a muffle furnace heated to bright redness; the object of the asbestos pad is to protect the inner crucible from radiation from the roof of the muffle, and to insure that distillation shall not commence before the mixture in the outer crucible has time to heat up. Distillation commences in about two minutes, and as soon as a flame appears the asbestos may be removed. To insure complete oxidation of carbon the roasting should be continued for two hours. The mixture is then brought into water, the sulphides, etc., oxidized by bromine, and the solution acidified, filtered, and precipitated by barium chloride as usual. If the amount of sulphur is small it is advisable to allow the solution to stand on the water bath for 24 hours before filtering off the barium sulphate."

"It was suggested that as about 22 gms. of the lime-soda mixture was used, the large amount of calcium and sodium chlorides in the solution might affect the result. A

**Jour. Soc. Chem. Ind.* Dec. 15, 1905, p. 1212, V. 1. XXIV.

†*Jour. Amer. Chem. Soc.* 1898, 20, 882; *Jour. Soc. Chem. Ind.*, 1899, 77.

solution of pure sulphuric acid was therefore prepared of such a strength that 25 c. c. contained 58.8 milgms. of H_2SO_4 or 18.4 milgms. of sulphur; 25 c. c. of this solution was added to 20 gms. of the mixture, and worked up as usual, when 0.1428 gms. of Ba SO_4 was obtained, corresponding to 60.0 milgms. H_2SO_4 or 18.8 milgms. of sulphur."

In reply to a letter (1906) asking what method he used for the determination of sulphur, Dr. C. F. Mabery replied: "There is only one method for the determination of sulphur in oils and asphalts that is reliable, and that is combustion in a current of oxygen and titration in alkaline solution. The only way to apply it is a glass tube as long as a combustion tube. The products are absorbed in a 1/10 or 1/100 normal caustic solution. I have had hundreds of analyses made in the last six months by this method. It is reliable to within a few hundredths of 1 per cent. The trouble with all fusion methods is that volatile sulphur compounds escape as decomposition products."*

Lidow changes the oxidation treatment by using a sodium nitrate mixture. He dissolves 1 gm. of the bitumen with chemically pure ether or some other volatile solvent, and mixes the solution in a mortar with 30 gms. of a mixture of 17 parts potassium nitrate and 13 parts soda (sodium carbonate?). The solvent is evaporated, the mixture projected into a platinum vessel of 250 to 300 c. c. capacity at a bright red heat and the sulphur determined in the melt as usual with barium chloride. According to Pellet (*Zeitsch. f. Angew. Chem.* 1900, p. 811) it is important that the heating be done over a flame free from sulphur (alcohol, benzine, etc.).†

Instead of the sodium nitrate mixture, Eschka employs a mixture of calcined magnesia and ammonium nitrate, a method which Hodgson prefers to all others for accuracy and convenience.‡

Henriques combines the oxidation of the substance by means of nitric acid in an open vessel followed by a fusion with a sodium nitrate mixture, and can recommend this

**Jour. Am. Chem. Soc.* 1894.

†*Jour. Russ. Phys. Chem. Ges. zu St. Petersburg.* 31, p. 567; *Zeitsch. f. Angew. Chem.* 1898, p. 296.

‡*Jour. Am. Chem. Soc.* 1898, p. 882. *Zeitsch. f. Angew. Chem.* 1898, p. 1141.

method as unqualifiedly and technically the most convenient. One gm. of the sample to be analyzed is placed, with a glass rod in a small unglazed porcelain dish of 6 c. m. diameter and 30 c. c. m. capacity, which is then filled one-third full with pure concentrated nitric acid (sp. gr. 1.4) and warmed on a water bath. He then covers with a watch glass and continues warming until brisk evolution of red fumes shows the beginning of the decomposition. The reaction under the watch glass should be carefully watched that it does not become too violent, in which case the dish should be removed from the water bath or the heat lowered. The process is thus kept wholly in hand. The heat is applied to the covered dish from time to time until the substance is wholly decomposed and the evolution of red fumes ceases. The watch glass is then removed, and wiped with small pieces of filter paper, which are dropped in the acid and the acid evaporated to the consistency of a syrup. Then a quantity of nitric acid is added equal to that first taken, and evaporated a second time, which is in all cases sufficient.

When the nitric acid is driven off, the warm syrup is completely mixed with not to exceed 5 gms. finely pulverized sodium nitrate mixture (5—3) that must be so carefully introduced as to exclude large crystals of nitrate.

It is left upon the water bath until no more carbonic acid escapes and finally there is strewn over the matted mass more sodium nitrate mixture before the final melting. This has to be done with care to avoid spattering.

The melting dish is placed about 5 cm. above a small Bunsen flame, which can later be made higher, covered over with a second dish of the same form (concave surface down). The spattering will increase, but the sodium nitrate that strikes the cover will remain there in small particles. Under normal conditions the mass gradually blackens at the edges and can become strongly melted while the brown products of distillation collect on the cover dish free from sulphur. The duration of the melt can be diminished towards the end by removing the covered dish and by stirring with the glass rod held by crucible tongs for 1 to 1½ hours.

After cooling, the melt is treated with boiling water and filtered, by which the sulphuric compounds go over into the

filtrate as alkaline sulphates, while upon the filter are found the metals present in the form of carbonates or oxides.*

Nearly all asphalts contain silicon (see Le Bel and Muntz, *Bull. Soc. Chem.* (2) 17, p. 156; Le Bel, ditto, (2) 50, p. 359), in the form of organic compounds. In practice the filtrate is evaporated to dryness with addition of hydrochloric acid and the silicic acid becoming insoluble, is drenched with water and filtered off. The sulphur is finally determined in the form of barium sulphate as usual.

By another procedure the asphalt is treated by melting with a mixture of sodium carbonate and caustic soda, and the sulphides present are oxidized with sodium peroxide and the sulphur precipitated as barium sulphate.

v. Konek likewise uses sodium peroxide for the determination of sulphur in bituminous and all organic bodies, and concludes the work by the well known sodium peroxide calorimeter of Parr.† The determination in this apparatus, as compared with other methods, requires so short a time, that the process of v. Konek has been called the rapid method for the determination of sulphur. A detailed description of Parr's calorimetric researches and of his method of procedure is given by G. Lunge (*Zeitsch. f. Angew. chemie* 1901, p. 793).

The determination of the calorific value is never applied to asphalts. For the purpose of determining the sulphur the bomb is taken from the water bath of the calorimeter, the cover unscrewed and finally well rinsed with cold water into a Becker glass of 700 c. cm. capacity. The open bomb is then placed in an inclined position in the Becker and in order to decompose the contents, 10 c. cm. of cold water are added thereto and the glass covered with a close fitting watch glass. In a few minutes the steel cylinder froths, and boiling, pours the greater part of its contents into the Becker glass. After the first strong reaction is over the hot bomb is raised out of the beaker with a pair of crucible tongs, placed in a small porcelain dish and rinsed at first with a little cold water until it no longer has an alkaline reaction, when the small piece of iron wire which serves to ignite the mixture of peroxide of sodium is washed out of the bomb. Wash sparingly with

**Jour. Am. Chem. Soc.* 22., 1899, p. 802.

†*Jour. Am. Chem. Soc.* 22, p. 646. *Chem. Zentralblatt*, 1900. II. 10 50.

water so that with the additions there shall be no more than 200 c. cm. In this way the united contents of the bomb are estimated in the Becker glass, which, containing in solution sodium peroxide, sodium carbonate and sodium sulphate, will be found strongly alkaline, and must be neutralized with 40 c. cm. pure concentrated hydrochloric acid, heated to boiling, under a watch glass, freed from any particles of carbon or other impurities by filtration, the boiling filtrate precipitated in the usual way with barium chloride, and the sulphuric acid found. The primary condition of the use of Na_2O_2 in the determination of sulphur is, that it be chemically pure, and, above all things, absolutely free from sulphur compounds.

In the determination of the sulphur content of asphalt by the use of the "rapid" process, the practically small quantity of the substance is weighed, by pouring it from a crystallizing dish in which the bitumen has been rendered sufficiently fluid by warming it to 70° to 90° . Harder asphalts are brought into the form of powder. Sometimes one-half the mass of the Na_2O_2 is warmed in a drying oven and 0.3 to 0.4 gm. of the melted asphalt is allowed to drop upon it, then mixed as well as possible and the mixture brought while warm into the bomb by means of a small copper funnel; the second half of the peroxide serves to rinse the dish, glass rod and funnel, and then, after strewing the surface with 0.1 to 0.2 gm. pure, dry, powdered tartaric acid, the bomb is closed and discharged as described. The decomposition of the contents of the bomb with water requires much circumspection, because the mixing of viscous substances with Na_2O_2 is not possible without more or less lumpiness. Moreover, the coal occasioning the explosion is free from sulphur, as v. Konek has pointed out, because this, even with sodium peroxide, is much more quickly oxidized than as carbon.

Following are the results of analysis, conducted by this method:

	Percent of Sulphur	
	Rapid	
	Method. Carius.	
1 Bitumen from Trinidad (old sample).....	3.52	
2. Bitumen from Trinidad (new sample).....	3.56	
3. Bitumen from Derna Tartaros, Hungary.....	0.56	0.30

v. Konek commends as the chief excellence of this method the rapidity and consequent saving of time. In many cases the circumstance is naturally also of great value, that at the same time therewith the determination of the molecular, calorific and heating effects, can be associated with it. In from 10 to 20 minutes, the sulphur content of every organic compound is quantitatively separated in the form of barium sulphate, a result that no single one of the hitherto useful methods for the determination of the sulphur in organic bodies has accomplished.*

Mabery burns crude petroleum, asphalt, etc., in a stream of oxygen or air and leads the products of combustion through a standard solution of caustic potash. The sample to be examined is put in a platinum boat in a wide potash glass tube, burned in a stream of air or oxygen gas and the gas with a steady stream of carbonic acid led through into normal caustic potash in a tube filled with pieces of glass. After the determination of the combustion, by the application of methyl orange, an indicator not affected by carbonic acid, the solution is titrated back, and from the consumption of the normal solution, the sulphur content of the burned product may be calculated.†

For determining sulphur J. Heusler, C. Engler, R. Kieszling and Ohlmüller burn the oil in a small lamp and absorb the gaseous products of combustion in an absorbent fluid, like solution of permanganates (Heusler, Kieszling) an alkaline bromine solution (Engler) or hydro-potassium carbonate solution (1-20, Ohlmüller).

These four methods were subjected by S. Friedlaender to comparative tests, who found that in respect to accuracy the results are equally complete and reliable. A prerequisite is a perfect sootless combustion as well as an efficacious absorbent for the gas. If, according to the method of Holde, the asphalt be dissolved in a petroleum free from sulphur, and burned in a lamp, then this method can also be applied with success to the determination of the sulphuric content of asphalt.

Neither of these lamp processes is recommended for

*Zeltsch. f. Angew. Chem., 1903, p. 516.

†Am. Chem. Jour., 1854, p. 544.

solid bitumens by the author, but the process of Engler is given as that which in practice may be found most useful and refer, regarding the others, to the dissertation of Friedlaender.

The sample of petroleum, or a solution of the sample of asphalt in petroleum, is filled into a small lamp (Fig. 1), which is connected with the air tight cylinder *C* by means of the cork stopper *K*. The cork stopper bears a metal cap *M*, through which the air required for combustion is led through

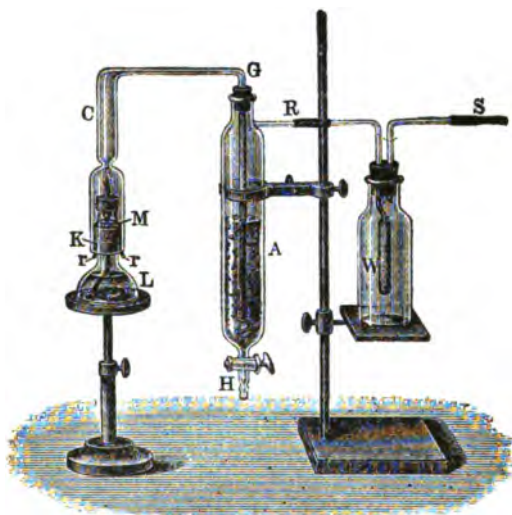


Fig. 1.—Engler's Lamp.

the pipes and into the combustion chamber; the metal cap terminates in a perforated plate by which the air is equally distributed. Into the cylinder a glass tube *G*, bent at a right angle, is fused through which the products of combustion are drawn into the absorbent vessel. This vessel is half filled with glass beads and will hold from 20 to 25 c. cm. of the absorbent fluid. To the absorbent vessel is attached a Munich wash flask, to retain any of the absorbent fluid that may escape from the absorbent vessel through too rapid transmission of the air. The gas that is not absorbed is removed by a suction pump through the escape pipe *S*.

At the end of the combustion, 20 to 25 c. cm. of water are sucked into the absorbent vessel through the cock *H*, and a minute thereafter air is aspirated through the whole apparatus and the water again drawn off; this operation must be repeated several times.

According to the representation of Engler the most useful absorbent fluid is a 5 per cent solution of potassium carbonate containing sufficient free bromine to give a slightly yellow color to the liquid, which is left to stand a few days in the air, as a stream of sulphur free air is passed through it, until it is discolored. A portion of the colorless solution is tested by acidulating with hydrochloric acid and precipitating with barium chloride solution, if the presence of sulphuric acid is surmised, and the remainder that is found free is applied to the absorption of the gases of combustion.

At the end of the combustion the discharged fluid is saturated with hydrochloric acid, and boiling hot, is precipitated with barium chloride.

Table I shows the duration and the results of the four methods as applied to the same petroleum:*

Method.	Application.	Duration of Combustion.	Percent of sulphur.
Heusler	13.86	2 hrs. 20 min.	0.0286
Engler	11.05	4 hrs. 56 min.	0.0286
Keisling	11.71	2 hrs. 04 min.	0.0280
Ohlmüller	12.74	hrs. 31 min.	0.0284

Not only can the free sulphur involved in the bitumens of natural asphalt, but also that combined in organic forms as well, be made to appear. According to Endemann, it is not immaterial which solvent is used for the extraction of bitumens. In treating the free sulphur contained in residues he casts aside carbon disulphide and all solvents containing sulphur and carries on the extraction with pure chloroform.

The determination of nitrogen in solid bitumens is frequently a matter of much importance.

The presence of this element in bitumens was first suspected by myself in 1866, when I observed in California a pool of crude petroleum filled with maggots. Early in 1867

*Heusler, *Zeltsch. f. Angew. Chem.* 1895, p. 285. Engler, *Chem. Ztg.* 1896, p. 197. Kieszling, *Ditto*, 1896, p. 199. Ohlmüller, *Arb. aus dem Kaiserl. Ges.-Amt, Berlin*, 1899, XV, p. 366. Friedlaender, *Chem. Ind.*, 1899, p. 343. Holde, *Lunge, Chem. Techn. Untersuchungs-methoden*, III, p. 34.

I determined by the soda-lime process the percentage of nitrogen in California bitumens and found an unexpectedly large amount in those samples that had been least subjected to influences that might produce changes in them.

When in California in 1894* I showed that nitrogenous basic oils existed in all of the semisolid and solid bitumens occurring in southern California that were examined by me and from widely separated localities. Since then, Mabery and others have discovered and determined nitrogen in many forms of bitumen from different parts of the world.

In a paper published in the *Jour. Soc. Chem. Ind.*, June 30, 1900, Dr. C. F. Mabery says:

"Nitrogen may be detected in almost any petroleum, but usually in minute quantities.

"The amount found by Beilby in Pennsylvania petroleums was 0.08 per cent, and in Russian oil 0.05 per cent. Since we have found it impossible to determine nitrogen by any other method than by combustion, measuring the volume of nitrogen, I am unable to see how those minute quantities were determined. The Kjeldahl method evolves only a part of the nitrogen as ammonia, since permanganate evolves only a part of the nitrogen as ammonia and a part as nitrogen.

"Japanese petroleum from some fields contains almost as much nitrogen as California oil.

"A large proportion of nitrogen in California oil was early recognized by Peckham, who stated that the proportion varied between 0.56 and 1.10 per cent. In 1892 Salathé found proportions of nitrogen varying between 0.75 and 3.5 per cent.

"To ascertain the proportion of nitrogen in California oils a number of specimens of crude oil, kindly furnished direct from the wells by Mr. Clifford Richardson, were burned in a combustion tube and the nitrogen measured. Also in the same specimens nitrogen was determined by the Kjeldahl method.

Sixteen specimens were examined. The first four are given as an illustration, in Table II.

**Am. Jour. Science*, Sept., 1894.

Source..	Nitrogen by Kjeldahl.	Nitrogen by volume.
Summerland oil	0.88 per cent	2.10 per cent
Los Angeles Field, Eastern District	0.47 per cent	1.42 per cent
Torrey Canon, Venture Co...	0.64 per cent	1.91 per cent
Wild Bull Gulch, Venture Co.	0.71 per cent	2.39 per cent

Dr. Mabery continues:

"In the Kjeldahl determinations the oil was heated until the solution became light yellow with complete oxidation of the crude oil.

"These large percentages of nitrogen show that the nitrogen compounds constitute a considerable portion of the crude oil. * * * Assuming that the average molecular weight of the bases is represented by the formula $C_{10} H_{13} N$, which is probably too low, the percentage of nitrogen should be multiplied by 10, which would give between 10 and 20 per cent of the nitrogen bases in the crude oil.

"The bases which formed the basis of this examination were separated from California distillates by Peckham and Salathé, by washing a large quantity of the distillates with dilute sulphuric acid, and precipitating the base with alkali. Portions of these basic oils were kindly placed at my disposal by Professor Peckham."

The oils examined by Dr. Mabery were obtained in the refinery of the Union Oil Co. of California in 1894, by washing 100 barrels of a distillate from crude oil, technically known as "40° distillate," with 100 pounds of oil of vitriol diluted with nine times its volume of water. This acid solution was saturated, and tasted bitter and not sour. A second treatment with the same amount of acid and water obtained a solution only partially saturated. The saturated solution was neutralized with a solution of sodium hydrate and the separated precipitate of basic hydrates was dissolved in a petroleum distillate nearly as volatile as gasoline. It was supposed that the naphtha could be separated from the bases by steam as the naphtha had been distilled from a less volatile distillate by steam. The first distillate by steam came over colorless but it was contaminated with the basic oils and possessed their familiar odor. Only one-half the naphtha used could be distilled by steam. On applying direct heat, the naphtha in the distillate decreased until finally the basic

oils came over pure, at first of a brown color, then transparent and of a cherry red color, and lastly greenish brown, and heavier than water, through which the drops sank like shot. The distillation was continued until nothing came over at a temperature near the red heat. A dry residue, resembling coke, remained in the still, a part of which was soluble in hydrochloric acid, from which solution sodium hydrate precipitated cream colored flakes. The red and brown oils were readily dissolved from solution, as also in a pure state, by hydrochloric acid. Dr. Mabery was furnished with a mixture of these oily distillates and a dilute sulphuric acid solution of the whole series from the lightest to the heaviest.

An examination, in less detail, was made of all the forms of bitumen occurring in the region south of the line which forms the northern boundary of San Luis Obispo, Kern and San Bernardino Counties; with a result that every form of natural bitumen and their distillates, whether fluid, semifluid or solid, yielded qualitative tests that indicated the presence of compounds, soluble in dilute acids and possessing the peculiar odor of these basic oils. The petroleums and malthas of the Santa Clara valley, Ventura Co., the asphaltums formed on the surface by their decomposition from natural causes, and the asphaltums from veins near Santa Barbara and at Asphalto, in Kern Co., all gave the same reaction.*

The method which I have employed for testing solid bitumens for nitrogenous basic oils is as follows: Ordinary kerosene is washed with concentrated sulphuric acid, decanted from the acid and then washed with dilute sulphuric acid, then with ammonium hydrate and dried by agitation with plaster of Paris. The oil when purified in this way is beautifully transparent and colorless and is perfectly inert to the action of dilute sulphuric acid.

The semifluid maltha or asphaltum in powder is thoroughly agitated with about ten times its bulk of the purified kerosene and after solution is effected an equal bulk of dilute (1-9) sulphuric acid is added and the whole thoroughly shaken. The operation can best be conducted in a graduated

*Am. Jour. Science, Jan., 1894; Ibid, Sept., 1894; Jour. Franklin Institute, Nov., 1895; Proc. Am. Philos. Soc., Vol. xxxvi, 103, 1897; Jour. Chem. Ind., Vol. xix, June, 1900.

stoppered cylinder, of about 25 c. cm. capacity. After several shakings, the mixed liquids are allowed to rest, when the kerosene solution will float above the dilute acid. A convenient portion of the acid solution is then removed with a pipette and introduced into a second jar, where it is neutralized with a solution of sodium hydrate. If any considerable amount of these compounds are present they will float on the surface of the liquid; smaller amounts will give their peculiar odor.

Oxygen is estimated by difference. This is a very uncertain and unsatisfactory procedure. It approximates accuracy only when all of the other constituent elements have been carefully determined, as it is obvious that all the losses and errors accumulate in the residual difference between the sum of the percentages of known elements and one hundred per cent.

CHAPTER XI.

THE PROXIMATE ANALYSIS OF SOLID BITUMENS.

As is the case with all other methods of chemical investigation, the investigation of bitumens, as at present conducted, represents a growth. The starting point is the classical research of Boussingault, first described in 1837.*

It must be remembered that this research was undertaken more than seventy years ago, when organic chemistry was in its infancy as compared with to-day, and when the methods of investigation with which the chemists of to-day are familiar were unknown. It detracts nothing from the value of Boussingault's work to say that it is worthless as a guide in modern research.

I have found by years of experience that solid bitumens cannot be investigated by ordinary methods of distillation. They are decomposed at temperatures much below that at which any portion of them becomes volatile. I have distilled them in California and elsewhere under the most diversified conditions with one uniform result. Under atmospheric pressure, with any of the various forms of retort that I have used, only products of destructive distillation can be obtained. These products vary in character with the crude material. Trinidad pitch, either lake or land, is decomposed when heated to a temperature of 100° C. with a copious evolution of hydrogen sulphide. Whether or not this reaction would attend distillation in vacuo I do not know.

When I first made a laboratory examination of California bitumens, which were both fluid, semifluid and solid, I contrived an apparatus which to answer my purpose had to fulfill the following conditions. It should be capable of working not more than one and one-half liters, and admit of being heated by an ordinary gas furnace. The joints should sustain a pressure of 40 lbs. per sq. in., and it should be so constructed as to admit of the ready extraction of the coke. I

*(*Ann. de Chem. et de Phys.* (2), LXIV, 141, p. 91.)

could find no description of any such apparatus, but after numerous failures and corrections I found my want so well and fully supplied, that I am led to offer a description, for the benefit of those who, like myself, have felt the need of such an instrument.

Upon each extremity of a piece of wrought iron gas-pipe, 3 ins. in diameter and 20 ins. in length, a cap is securely screwed. The caps should be heated nearly to redness and screwed on to the cold pipe in order that by their contraction they may be more firmly secured. The pipe is then put in a lathe and the caps turned off in such a manner as to leave a band upon each end of the pipe, about $\frac{3}{4}$ in. in width, and two circular discs of iron, each about 4 in. in diameter, and $\frac{1}{4}$ in. in thickness, having a projection upon one of their surfaces to which a wrench may be applied. The edges of each extremity of the pipe with the bands are now carefully turned off, presenting smooth surfaces slightly beveled inwardly. The plane surface of each of the discs is then so turned off upon its circumference, that it will exactly fit the beveled edge of the pipe. This completes the retort.

A stout parallelogram is then made half an inch longer and wider than the retort, one of the shorter sides of which should contain in the middle a stout set-screw, and the other an orifice made to fit the projection upon the disc. This may be called the frame.

Two holes are then drilled a short distance from either extremity of the retort, in a line parallel to the axis of the retort, and plugs fitted to them. One of these should admit a $\frac{1}{2}$ -in. and the other a 1-in. gas-pipe. With this arrangement the retort may be used either for pressure distillation with a valve, or for distillation by the ordinary process. It also admits of being connected with an apparatus for furnishing superheated steam or carbonic acid gas, either of which are sometimes used to assist the distillation of hydrocarbons. Both the goose-neck and valve should be connected with the retort by a short piece of gas-pipe and a brass "union" or coupling, as the difference in the expansion of brass and iron would cause a joint of the two metals to leak very badly when subjected to a high temperature. The goose-neck may be made of the ordinary form, tapering

from 1 in. to $\frac{1}{4}$ in., and about 10 ins. in length. The material should be copper, brazed.

In order to use the retort the plugs are inserted, one of the discs is luted with a very thin paste of plaster of Paris and firmly pressed into its seat. The retort is then slipped into the frame and left a moment for the luting to set, the open end being uppermost. The oil is next poured in and the other disc luted into its seat, the frame adjusted and the set-screw firmly set up, so as to securely fasten both discs in their places. The goose-neck or valve is then adjusted, and the connections made with the worm and receiver. It will be observed that all the expansion that takes place in this retort brings the different portions of the apparatus more firmly together, instead of causing them to crack apart and leak with every slight variation of temperature, as is usually the case. With this arrangement I was able to distill 1500 c.cm. of petroleum to dryness, the last portions coming over at a red heat. The distillation was commenced with two ordinary Bunsen gas lamps, increased as required to four, and toward the end of the operation to six—the latter number being sufficient to bring the side of the retort in contact with the flame to a bright cherry-red heat.*

The apparatus is equally convenient for distilling small quantities of semifluid and solid bitumens; but while such examinations by distillation are sometimes desirable they are at present not to be considered in any sense analytic. The most elaborate, as well as the most successful research upon solid bitumens in which this method was employed was described by Mr. Clifford Richardson in *The Jour. Soc. Chem. Ind.*, Jan. 31, 1898.

The methods of analysis by solution remain. Solution may certainly be properly considered a chemical reaction, and the more solvents that can be applied to a solid with clearly-defined results that can be repeated with accuracy, the more complete must be the method of analysis. To dissolve a bitumen in carbon disulphide, which is a universal solvent for bitumens, does not analyze the bitumen, although it may separate the bitumen from its impurities; but to subject a bitu-

**Am. Jour. Science* (2), xlv, 230; *Chem. News*, xvi, 199.

men to the action of several solvents in succession, by which the bitumen can be referred to a distinct class, is a valuable analytical process.

These considerations have been impressed upon my mind during the several years last past, in which I have been attempting to arrange a process of analysis that shall apply to all bitumens, and enable the analyst to distinguish, both alone and in mixtures, the several varieties of bitumen, in a manner similar to the schemes that have been proposed for alkaloids or other organic compounds.

The subject is still under discussion and much remains to be done in perfecting details which must be frequently modified to suit special materials and special conditions. Parianite or Trinidad pitch is about as complex as any bituminous material submitted to analysis and it is selected for a detailed description of analysis by solvents for the purpose of showing not only what has been accomplished but what remains to be accomplished in this particular form of research.

Parianite may be regarded either as an emulsion of gas, mineral water; bitumen, that is, compounds of carbon, hydrogen and nitrogen, oxygen and sulphur, any or all of the last three, with organic matter not bitumen, and mineral matter consisting of silica and clay as impurities; or, it may be regarded as an emulsion of gas, water holding mineral salts in solution, bitumen as above described, with complex organic salts of iron, alumina, lime and magnesia, with ulmic and perhaps other acids, with amides and amines, with ferrous sulphide, and silica, some portions of which are in combination with the other ingredients and the remainder free. Either alternative exhibits a very complex substance, but each quite unlike the other. By what means can it be determined of what the mixture really consists? Certainly not by any process that separates a hypothetical substance called petrolene and a second called asphaltene, a third called organic matter not bitumen, and a fourth called mineral matter. One might just as well analyze a log of wood by burning it into smoke, flame and ashes.

THE GAS.

We will begin at the lake with the gas. I visited the lake on Point La Brea on four different days, and practically

walked all over the deposit, both inside and outside the lake. I did not once recognize the odor of hydrogen sulphide. When I was in California in 1865, it was stated that the big spring on the upper Ojai plateau discharged carburetted hydrogen. I found the gas would not burn, and then I gathered some of it and found it was nearly pure carbon dioxide. I suspect that the greater part of the gas discharged from the lake is also carbon dioxide. It is the normal product of the deoxidation of the sulphates contained in the lake water, as sulphuric oxide yields more oxygen than is sufficient to convert the bases present into carbonates. No doubt the deoxidation of the sulphates in the water is attended with a variety of reactions resulting in a variety of chemical products, of which both carbon dioxide and hydrogen sulphide form a part. The proper place to investigate these gases is at the lake.

THE LAKE WATER.

Mr. Richardson has fully investigated the lake water, and in his report in 1892 he gives his results in great detail. The water used by him was taken from the water floating on a kettle of melted pitch that was being refined. It was probably more highly concentrated than lake water, and had, perhaps, lost some of its volatile ingredients. He gives the following analytical results:

	IN ONE KILOGRAM.	Grams.
Cl		6.7757
SO ₃		5.5409
SO ₂0467
S ₂ O ₃		trace
H ₂ S		trace
S		trace
SiO ₂0688
B ₂ O ₃0117
I0008
Br		trace
P ₂ O ₅		none
Na		6.5149
NH ₄4071
K3391
Li0271
Ca5280
Mg2666
Fe0720
Al		trace
Mn		none
Cs & Rb		none
Organic4901
Oxygen		none
		<hr/> 21.0896

It is probable that these results indicate but do not represent the composition of lake water. They also indicate the composition of the water saturating the pitch. This water, examined by Mr. Richardson, has an acid reaction.

In a paper published by Mr. Richardson (*Jour. Soc. of Chem. Industry*, January, 1898), he gives an analysis of water from a spring that arose in the pitch:

IN ONE KILOGRAM.

	Grams.
Specific gravity.....	1.0599
Solids at 110° C.....	82.100
Sodium, Na.....	27.193
Potassium, K.....	0.528
Chlorine, Cl.....	38.210
Sulphuric acid, SO ₃	3.207
Calcium oxide, CaO.....	trace
Magnesium oxide.....	0.506
Carbonic acid, CO ₂	3.700
Silica, SiO ₂	0.222
Organic matter.....	?
	<hr/>
	73.566

From these analyses it appears that the lake water is rich in chlorides and sulphates of sodium and iron, with iodides, bromides and borates, in the first instance, and carbonates in the second.

AQUEOUS SOLUTION OF THE PITCH.

One hundred grams of a fine specimen of commercial lake pitch were digested with successive portions of distilled water at a temperature of 60° to 70° C., until there was no longer a reaction for either Cl or SO₃. The first portion contained a large amount of ferrous sulphate. The solution, on standing, deposited a small amount of ferric oxide. The solutions were concentrated to 1 liter and portions of 100 c. cm. were evaporated over a water bath. The residue contained chloride and sulphate of iron and sodium. Probably a larger portion would give reactions for all the soluble salts obtained by Mr. Richardson from lake water. This residue also contained a small amount of organic matter that was not determined. The percentage of this residue was 1.135 per cent. of the pitch.

THE ALKALINE SOLUTION.

It is impossible to visit the pitch lake without observing that an immense amount of partially decayed vegetation is entombed in the pitch. Enormous stumps are uncovered, with trunks and branches of trees in every stage of decay, from solid wood to large masses of humus that a kick will scatter, precisely as if they were found in the peat of a bog. This humus becomes kneaded and incorporated with the pitch precisely as is the mineral matter, and, what has not been properly recognized, the humus on a colossal scale has formed those peculiar compounds, the precise natures of which are but little known, but which Mulder, Boussingault and others have referred to amides and double salts, in which ammonia, the peat acids and iron, and especially alumina, are combined into exceedingly complex compounds, insoluble in water, but readily yielding to solutions of alkaline hydrates and carbonates. These reactions are brought together from many researches and admirably treated by Prof. S. W. Johnson in his "How Crops Feed," pp. 276-280, to which the reader is referred. The treatment there recommended to be applied to soils for the determination of the humus compounds has been applied to this sample of Trinidad pitch with the most satisfactory results, and a flood of light is thrown upon the problems presented by these unique and complex substances. 4.9325 gms. of the dried residue which represent 5,000 gms. of air-dried pitch, were digested in successive portions of a solution of dry sodium carbonate, 5.3 gms. to 1 liter of distilled water. The first portion was colored as dark as port wine and the last portion was uncolored. The alkaline solution was acidulated with hydrochloric acid and the precipitated ulmic acid was collected on a balanced filter, dried at 100° C. and weighed. The ulmic acid represented 1.542 per cent of the pitch. The residue from the sodium carbonate solution was then boiled with a dilute solution of sodium hydrate and the dissolved ulmin was precipitated with hydrochloric acid in considerable amount.

The acid solutions were neutralized with sodium hydrate, acidulated with acetic acid and the aprocronic acid precipitated with acetate of copper. Only a trace of crenic acid was

precipitated by ammonia. This might reasonably be expected, as crenic acid is being continually converted to apocrenic acid by contact with reducing substances, of which bitumen is a notable instance. I am inclined to think that Prof. S. W. Johnson's observation, that ulmin represents only the ulmic acid of difficulty decomposable ulmates, is correct ("How Crops Feed," p. 225, note). It is well known that ulmic acid and ulmin have the same composition, but the first is readily soluble in Na_2CO_3 , while the latter requires prolonged boiling with NaOH for its solution. I believe that the ulmin represents only the ulmic acid that is in combination with alumina and iron, which compounds are decomposed with considerable difficulty.

Wiley, in his "Principles and Practice of Agricultural Analysis," Vol. I, p. 28, recommends for the determination of humic and ulmic acids the use of the Huston-Grandcau method, as follows: 10 gms. of the soil are washed with a 3 per cent solution of HCl , and then washed into a 500 c. cm cylinder with a 4 per cent solution of ammonium hydrate. Shake and let remain in a horizontal position for 36 hours. Determine the humus in an aliquot part. This is, no doubt, a very good method for ordinary soils containing free peat acids and their salts of lime and magnesia; but, used on No. 8, the amount of ulmic acid obtained was only 0.044 per cent against 1.542 per cent obtained by the sodium carbonate method. In Parianite the peat acids are, no doubt, combined with iron and alumina, as only traces of lime and magnesia were found in the HCl solution.

The ammonia that has been observed escaping from kettles of melted pitch when it is refined is, without doubt, derived from the amido compounds referred to above. The relation which the pitch bears to a soil is strikingly shown in the luxuriant vegetation that covers the pitch wherever it is not in motion. Outside the lake a tropical jungle grows, with its roots penetrating the pitch and forming a sod of great tenacity, which often renders tons of the pitch worthless from admixture of vegetable matter. Such pitch is universally rejected.

THE DETERMINATION OF WATER.

The pitch is taken from the lake dripping wet. It begins to dry out immediately, but it requires a long time to completely remove the water if the lumps are unbroken. It is, however, easily dried if pulverized and placed in the sun. By thus drying to a constant weight the water may be determined.

Another method that I have found very convenient for determining water in semifluid or solid bitumens is to dissolve the bitumen in refined and recently purified (see page 190) illuminating oil and distil in an alembic or tubulated flask, collecting the distillate in a graduated cylinder and measuring the water, which may be estimated to weigh a gm. to 1c. cm. at 60° F. For this purpose, at least 50 gms. of the bitumen should be dissolved in 200 c. cm. of the liquid, and the distillation should be continued until no more water passes over.

PETROLEUM ETHER SOLUTION.

For this determination three washed filters should be balanced. In two of them should be weighed 1 gm. of the pitch. These filters should be placed in separatory funnels and exhausted with dry petroleum ether, of 74° B. or higher, as rapidly as possible. It is rare to find petroleum ether on the market, free from water; it should always be agitated with dry plaster of Paris before being used. The percentage of dry pitch dissolved by the petroleum ether will vary within narrow limits from 32 to 36 per cent.

If the petroleum ether solution be allowed to stand, it deposits a film upon the surface of the containing vessel beneath the liquid. This deposit is not a precipitate. If the vessel is of glass, the entire surface of the glass beneath the liquid is covered with the film, from which the liquid may be cleanly poured. This film readily dissolves in chloroform to a transparent solution. This chloroform solution evaporated to dryness over a water-bath gave 1.884 per cent of the pitch, of a brilliant black solid, which, when heated, melted, distilled, intumesced and burned to a very porous light ash that appeared to be alumina. The ash amounted to 41.508 per cent of the solid mass or 0.0782 per cent of the pitch.

If the petroleum ether soluble be treated in solution with fuming nitric acid, an orange-colored nitro derivative is obtained, from which the petroleum ether may be easily distilled. An examination of these nitro derivatives is a much more promising field for research than the products of distillation, contaminated as they are with the inevitable decomposition products of high temperatures.

THE TURPENTINE SOLUTION.

When in California, in 1894, I treated 100 gms. of lake pitch with boiling spirits of turpentine, and upon adding to the solution a large excess of petroleum ether, obtained a copious brown precipitate. I gathered this precipitate on a filter and washed it with petroleum ether, in which it is wholly insoluble. It is also insoluble in ethyl ether and ethyl and methyl alcohol. Heated in a platinum crucible, it yields a large percentage of ash. This ash consisted of:

Silica	—
Alumina	—
Iron	—

For a long time I supposed this precipitate was asphaltene. but on attempting to determine the sulphur in it I found it was an organic compound of silica and alumina. I have not yet completed my investigation of this material, which I believe is a double salt of alumina, containing ulmic acid.

More than 12 per cent of the precipitate may be dissolved in solution of sodium carbonate and a still larger percentage may be dissolved in a solution of sodium hydrate, from both of which solutions hydrochloric acid will precipitate an organic acid. This material also furnishes a much more inviting field for research than the decomposition products of distillation.

THE CHLOROFORM SOLUBLE.

When the residue left on the filter from treatment with boiling spirits of turpentine is treated with cold chloroform, a third portion is dissolved. The percentage varies with the pitch. In those analyzed by Miss Linton it varied in the five land pitches from 3.139 to 8.185, in the lake pitches from 2.137 to 7.222, and in those from the annular space from 4.800 to 6.900.

When the soluble is evaporated from the chloroform it forms a brilliant, black, hard varnish. Heated, the varnish melts, intumesces, gives off heavy vapors which burn with a smoky flame, leaving a red ash, consisting chiefly, if not wholly, of ferric oxide. In one instance a portion of this varnish yielded 0.779 per cent of this ferruginous ash.

This soluble is precipitated from its solution in benzole or chloroform upon the addition of an excess of petroleum ether, as a seal-brown powder. This precipitate may be washed with petroleum ether, ethyl alcohol or ether, in all of which it is insoluble. Analyses, that have been fully described elsewhere, and for which no claim for absolute accuracy is made, have shown this precipitate to consist of an organic sulpho-salt of iron (*Jour. Soc. Chem. Ind.*, December, 1897, No. 12, Vol. XVI). Here is also a more profitable field for research than is found among the decomposition products of distillation.

THE HYDROCHLORIC ACID SOLUTION.

Whenever limestone forms any part of a bituminous mixture, whether natural or artificial, it is essential that it should be determined. When crushed stone is used, some portion of it is usually soluble in hydrochloric acid. Gypsum is also dissolved by it, and may be detected by testing the solution for sulphuric acid. A very small percentage of the residue of Parianite remaining after solution in chloroform is soluble in a 10 per cent solution of hydrochloric acid. I have not ascertained what elements enter this solution.

THE RESIDUE.

That which remains on the filter after treatment with hydrochloric acid consists of cellulose and humus, mixed with such mineral matter as is not in organic combination in the pitch. The organic matter cannot be burned off without decomposing pyrite and burning out more or less of the sulphur, as the ash of the filter is usually saturated with ferric oxide in the form of colcotha. The proper procedure is to cut the filter in small pieces, mix these pieces with sodium carbonate and potassium nitrate and deflagrate. The silica, iron and alumina can then be determined while the sulphur appears as sulphuric acid, in the usual way. By determining the sul-

phur in another portion of the pitch in like manner and deducting the sulphur found in the residue from the whole amount of sulphur, the sulphur in organic combination can be ascertained. At the same time that this total amount of sulphur is determined, the total amounts of silica, alumina and iron can also be correctly determined. This correct total amount of mineral matter will be found to be considerably in excess of the amount found by the usual method of analysis by solvents; inasmuch as an appreciable amount of alumina and iron in combination with organic radicals pass into solution, which exist in the pitch dissolved in the bitumen, and which in the process of analysis pass into the solutions formed by the various solvents employed.

THE ORGANIC MATTER NOT BITUMEN.

Precisely of what this consists has not been determined. It is obtained by burning the residue that remains from the solution in chloroform, at a dull red heat. If the pitch is not finely pulverized, but is treated in coarse lumps, the residue from the chloroform contains fragments of vegetation of appreciable size. There is also a considerable amount of an exceedingly fine gray powder that is easily recognized as ferrous sulphide. A determination of the sulphur in this residue gave 0.8844 per cent of the pitch; this is equivalent to 9.793 per cent of the residue, or, 18.368 per cent of the residue of ferrous sulphide. These figures are suggestive rather than final.

In the ordinary method of analysis by solvents, with combustion of "organic matter not bitumen" and determination of the residue from the combustion, the organic matter not bitumen amounted to 8.507 per cent and the mineral matter to 32.243 per cent. How large a part of the organic matter not bitumen was sulphur cannot be conjectured; but no question can be entertained for a moment that a very considerable portion of the 3.639 per cent of sulphur is lost in that way. Whatever the amount may be, the total per cent of material that is not bitumen, obtained by solution, is 40.750, while the sulphur, silica, alumina and iron, by the direct method amounts to 43.989 per cent.

THE MINERAL MATTER.

This is the residue left in the crucible after the organic matter not bitumen has been burned off. It consists of grains of silica with a small amount of alumina and a much larger proportion of ferric oxide in the form of colcotha, which indicates that it is a product of decomposition, and that, too, of a substance that is very intimately mingled with the entire mass of the residue and even the fiber of the paper. The paper is as completely filled with anhydrous ferric oxide as if it had been previously soaked in a saturated solution of ferrous sulphate.

The average totals of this mineral matter in the seventeen specimens of normal crude pitch is 36.444 per cent. If, however, the mineral matter, that is, the silica, alumina and sulphur, are directly determined, they will amount to:

	Per Cent.
Silica	19.593
Iron and alumina.....	20.272
Sulphur	3.505
	<hr/>
Total	43.370
By solution.....	36.444
	<hr/>
Difference	6.926

This difference of nearly 7 per cent is certainly represented by constituents of the pitch, a part of which pass into solution in the solvents of the pitch and a part of which are volatilized as "organic matter not bitumen."*

Following the reading of this paper before the Franklin Institute of Philadelphia, of which the above description forms a part, were several very pertinent criticisms, from which I quote:

Dr. S. P. Sadtler stated that he was ready to admit the complexity of constitution of Parianite or Trinidad pitch as maintained by Professor Peckham, in that it probably contained some of the mineral bases in an organic combination whether we concede that the organic substance is really humic acid or not; that it was moreover, so unstable that it could not be heated directly without some decomposition.

*Jour. Franklin Institute, March, 1900.

However, he did not think that this complexity applied to all natural bitumens—he recalled the natural bitumen of Uvalde Co., Texas, which could be extracted from the limestone rock, in which it occurred naturally, by the use of a naphtha solvent; that the same was true of the natural bitumen of Santa Barbara Co., Cal., where the Sisquoc asphalt was extracted in that way; that he had analyzed a natural bitumen from Joplin, Mo., occurring in the cavities in the zinc-bearing rocks, which was also almost entirely soluble without residue in petroleum naphtha. With reference to Dr. Peckham's method of analysis of bitumens, he was not satisfied that turpentine was to be depended upon as a desirable solvent. It was obvious that freshly-rectified spirits of turpentine, and that which had been exposed to the air for a time as warm turpentine upon a filter and had in consequence become somewhat resinous, would have distinctly different solvent powers. He had had occasion, in connection with another matter, to test this difference between turpentine free from resin and turpentine carrying resinified products, and knew that it affected the solvent action notably. To use turpentine, therefore, one would have to note its optical constant so as to insure its entire uniformity.

Dr. Sadtler stated that he had at one time proposed acetone as a solvent in asphalt analyses in place of petroleum ether, because it could be had of fixed boiling point and perfect purity, but found that its solvent power varied from that of petroleum naphtha, and therefore no longer tried to use it as a substitute. What is wanted is a study of the action of a series of solvents of fixed purity upon different natural bitumens.

Dr. Wm. C. Day gave some results of determinations of nitrogen in Utah Gilsonite by the Kjeldahl method; upon which Dr. H. F. Keller remarked that more concordant results and certainly more reliable figures might be obtained by combustion of the material with copper oxide than is possible with the Kjeldahl method.

Mr. Alfred H. Allen, Sheffield, England (correspondence) remarked, I am rather struck by the absence of any elementary analyses of the products obtained.

To all of which the author replied:

The use of spirits of turpentine was first suggested by the directions given in the first edition of Allen's "Commercial Organic Analysis." It is directed there that the bitumen in European asphaltic rock be dissolved from the mineral matter in freshly distilled Russian turpentine. The turpentine should be freshly and doubly distilled. In any case the filter should not be digested in turpentine, which, poured upon the filter while hot, has been allowed to get cold. The stopcock in the funnel should be closed, the filter filled with boiling turpentine, the stopcock immediately opened and the hot turpentine allowed to run off as rapidly as possible. This should be repeated until the turpentine is discharged colorless. There are very great differences observed in the action of boiling turpentine upon asphaltums and bituminous minerals from different localities. In some cases the solution is as readily affected as sugar and water; in other cases the solution takes place much more slowly. The points made by Dr. Endemann and Sadtler are theoretical, not practical; any other solvent, as, for instance, any of the benzole series that will dissolve the material not soluble in petroleum ether, will yield this precipitate on dilution with a large excess of petroleum ether. I have digested this precipitate in dilute hydrochloric acid, then in a dilute solution of sodium hydrate, which became highly colored, and then obtained a copious precipitate of an organic acid, in brown flocks, when the sodium hydrate solution was acidulated.

It is true that on a large scale, the bitumen of the Uvalde County bituminous limestone has been extracted with petroleum naphtha, yet I have never found among the many samples of this rock that I have tested a single sample in which the bitumen was all soluble in petroleum ether. It is, however, practically, all soluble in boiling turpentine. On a large scale, the portion insoluble in petroleum ether is washed out of the rock by the solution of the remainder in the petroleum naphtha, and the purified bitumen consists of a mixture of the two solubles.

I have for some time been of the same opinion, so well expressed by Dr. Sadtler, that "What is wanted is a study of the action of a series of solvents of fixed purity, etc." I have

in hand the material for precisely this work, but have hitherto been unable to devote to it the necessary time.

I also recognize the force of Mr. Allen's remark concerning the absence of elementary analyses. The reason is that hitherto I have not been able to obtain the substances described in this paper under such conditions and in such quantity as to make ultimate analyses advisable. Ultimate analysis should follow the study of the action of solvents of fixed purity. I have for some time been studying the action of pure alcohols, both absolute and of definite dilution, as well as acetone, ethyl ether and chloroform separately and in series. There is work enough on these problems to fill the twentieth century.

In further illustration of the value of this method when applied to the practical examination of bitumens, we give below the results of an examination of Turrellite—the bituminous coquina found in Uvalde Co., Texas.

The mineral itself is a gray mass, apparently of shells, cemented together with bitumen. It is exceedingly tough and difficult to break—a property that is easily accounted for when the material is deprived of its bitumen by being digested in chloroform. The mineral residue is then discovered to be a coquina or shell limestone possessing considerable stability without the bitumen. The shells are cemented together, and the cavities of many of them contain rhombspar and fragments of other shells, showing that the shell rock had been formed before the bitumen was projected into it.

Analyzed by solvents, there were obtained the following results:

	Per Cent.
Soluble in petroleum ether.....	9.415
Soluble in spirits of turpentine, after.....	4.121
Soluble in chloroform, after.....	Trace
Soluble in dilute hydrochloric acid, after.....	84.894
Sulphur in residue.....	0.138
Silica and clay.....	1.432
	<hr/>
	100.000

The average total bitumen is 13.536 per cent., of which the petroleum ether soluble is 69.555 per cent, and the spirits

of turpentine soluble is 30.445 per cent. This gives a bitumen wholly soluble in spirits of turpentine, of which 69.5 per cent is soluble in petroleum ether—a very high-grade bitumen. Five gms. of the rock, analyzed in duplicate, gave an average of 1.13 per cent of sulphur in the rock; 1.13 per cent—0.1381 per cent found in the mineral residue, leaves 0.9919 per cent of the rock, of sulphur in the bitumen, or, of the bitumen 7.328 per cent.

Digestion for several days in water at 60°—70° C., yielded a solution containing 0.126 per cent of the rock, which consisted of a trace of organic matter and calcium carbonate. There were no sulphates soluble in water. The portion dissolved by dilute hydrochloric acid consisted of calcium carbonate with traces of magnesium, iron, and sulphuric acid. The insoluble residue remaining on the filter consisted of silica, clay, and very small grains of pyrites of appreciable size. Caustic alkalis were without appreciable action on the rock. Fuming nitric acid acted upon it with great energy, dissolving the mineral matter and converting the bitumen into a brittle, charred mass of carbonaceous matter. The bitumen extracted from this rock, when analyzed by itself, yielded

	Per Cent.
Petroleum ether	71.28
Boiling spirits of turpentine, after.....	28.72
	<hr/> 100.00

The results are nearly identical with those obtained from the rock. The sulphur in the bitumen amounted to 7.582 per cent. The bitumen is not acted on by water, strong acids, or alkalis. Fuming nitric acid converts it into a friable, carbonaceous mass.

The above described work is analytical, as far as it goes. It is admittedly very imperfect, but it tells, nevertheless, its story concerning the constituents of this bituminous rock. There is no reason for believing that there is any oxygen compound in the bitumen contained in this rock. The bitumen is very pure, and contains a very large percentage of sulphur. The bitumen contains only a trace of mineral residue when burned.

Following the suggestion of Dr. Sadtler, as to the use of solvents "of fixed purity," I have been engaged for several

years in the intervals occurring in the routine work of our laboratory in a research from the results of which a series of solvents might be selected with which to successively exhaust any bitumen that might be made subject to analysis. This research work has been repeatedly interrupted and while the results obtained have been unsatisfactory from their incompleteness they have been very satisfactory as far as they have gone.

The solvents selected were 95 per cent methyl alcohol, pure acetone, washed ethyl ether and pure chloroform. The alcohol was redistilled, the acetone was redistilled over pure, dry, sodium carbonate. The ether was used as purchased, and the chloroform was washed with concentrated sulphuric acid and distilled over pure, dry, sodium carbonate. The sample of Trinidad pitch used was brought from the lake by myself in 1895. It was first exhausted with distilled water in a large flask. The residue was dried, filled into the capsule of a Soxhlet apparatus, with ground glass joints, and exhausted with the alcohol.

It was then exhausted with the acetone.

It was then exhausted with the ether.

It was then exhausted with the chloroform.

The residue was dried.

The alcohol extract was a soft, brown, solid, possessed of great viscosity and without perceptible odor. In solution it was light brown in color.

The acetone extract was a dense liquid that scarcely flowed, of a deep cherry red color and forming cherry red solutions. Its viscosity resembled old balsam of fir or partially dried copal varnish.

The ether extract was a brilliant black, soft solid.

The chloroform extract was a dull, black, brittle solid.

The residue was a dull brown, pulverulent solid, resembling a dry peaty soil.

This residue gave a copious extract to ammonium hydrate that when precipitated with hydrochloric acid gave a brown flocculent precipitate, that when dried burned with explosive violence.

The extraction by means of the capsules was a very long, tedious, unsatisfactory process. The capsules did not hold

the finest particles of mineral matter and no certainty could be had that the solvent did not form channels through the mass leaving portions of the mass from which the extraction was incomplete. This method was defective in another respect. Boiling acetone dissolved a substance in small quantity that was deposited on cooling. It was a cream colored, brittle solid that has not been investigated. The chloroform solution deposited on standing a brown pulverulent solid in appreciable amount. This has not been investigated.

It was therefore determined to make an extraction without the aid of heat in a separatory funnel. The water extraction has been made with results very near those previously made. The alcohol extraction has been made with very satisfactory results. The acetone extract is nearly completed. The residue from the acetone extraction, that still retains both the ether and chloroform extracts, is a brown pulverulent solid without a suggestion of bitumen of any description.

CHAPTER XII.

THE TECHNICAL ANALYSIS OF SOLID BITUMENS.

INTRODUCTION.

Technical analysis may be applied to natural solid bitumens including bituminous rocks, to factitious solid bitumens, and to mixtures of natural and factitious bitumens; also to street surfaces, to street mixtures, to asphalt blocks and any other bituminous mixtures.

All natural solid bitumens contain besides their content of bitumen a greater or lesser amount of insoluble material, which is partly organic and partly mineral matter, from which the bitumens may be separated by solution or extraction. Factitious bitumens on the contrary contain little or no insoluble organic or mineral matter.

While the analysis of the above named classes of substances will be each considered separately, the determination of the total bitumen in any or all of them will first claim our attention. For the determination of this total bitumen a solvent is selected that will completely separate all of the soluble from the insoluble constituents of the substances analyzed, by the simplest and most direct operation.

Bitumen is completely soluble in chloroform, bisulphide of carbon, benzole and perhaps other homologues of benzole.

As a solvent, chloroform is to be preferred, as its odor is agreeable and it does not readily ignite; but bisulphide of carbon, while much more offensive, and very inflammable, is very much less expensive. Either of these liquids is very volatile at the ordinary temperature, and may therefore be evaporated from the dissolved bitumens without decomposing them or removal of the most volatile constituents of them.

While the two solvents mentioned are universal solvents for bitumens, there are bitumens that are wholly soluble in spirits of turpentine but this liquid can only be evaporated from the extracted residues with great difficulty; there are cases in which its use is to be highly recommended. Acetone

and alcohols also furnish valuable assistance in helping to distinguish bitumens from different sources.

METHODS OF DISTILLATION.

Reference is here made to the research conducted by Bous-singault in 1837 as the earliest attempt at this kind of analysis. See page (91).*

Endemann extracts petrolene from asphalt through distillation in a current of carbonic acid, at 225°—250° C. The distillate contains paraffine if any is present in the asphalt. He determines the petrolene in an asphalt by extracting 5 gms. with chloroform, filtering the solution and distilling off the chloroform in a weighed flask; drying the residue for half an hour at 120° C. He then heats 0.2 to 0.3 gms. of this residue in a porcelain boat 12 hours at 250° C. in a stream of carbonic acid gas. The loss he calls petrolene, the residue asphaltene.† The significance of these terms has already been discussed. (See pages 98 and 101).

Endemann further claims that if a chloroform solution of the total bitumens in an asphalt deposits a precipitate, it consists of the mineral salts of asphaltic acid. By means of filtering, drying and weighing the quantity can be estimated.‡

METHODS OF SOLUTION.

Le Bel extracts the bitumen with naphtha, which he distills off, and then precipitates the "asphaltene" in the concentrated solution with amyl alcohol. This precipitate may be dissolved in naphtha and precipitated a second time with amyl alcohol. The precipitate appears as a black resin from which ethyl ether will dissolve a red substance having the appearance of rosin. The substance insoluble in ether contains silica, iron, manganese and lime.§

Meunier places a suitable quantity of asphalt in a closed vessel, with a sufficient quantity of the solvent and after repeated shaking leaves it to stand for some time. The solution is filtered off through a dry filter and the contents of the filter washed with the solvent as long as the solvent is colored.

*Ann. Chem. et de Phys., LXIV, 171; XCIII, 442.

†Jour. Soc. Chem. Ind., 1896, XV, 222-298; XVI, 121-126; XVII, 1003; Chem. Ztg., 1896, p. 987.

‡Jour. Soc. Chem. Ind., XVI, 121; Chem. Zentbl., 1897; I, 781.

§Bul. Soc. Chem., L, 359; Wagner Jahresbericht, 1889, p. 17.

The solvent is evaporated or distilled, and the residue dried at 100° to a constant weight, preferably in a stream of dry carbonic acid gas, to avoid possible oxidation. By drying and weighing the contents of the funnel, an estimate may be made of the impurities contained in the asphalt. The composition of these impurities may be ascertained by means of qualitative and quantitative chemical analyses.*

R. Kayser separates the constituents of asphalt by means of successive extractions with alcohol (Sp. gr. 0.835), ether and chloroform, and obtains substances that are quite different in both composition and properties.†

Capt. Dolphus Torrey has described a number of experiments with solutions of asphalt in alcohol. He found that alcohol at different temperatures was readily saturated with a portion of the asphalt that was partially deposited in a red precipitate when the solution cooled. The alcohol remained cloudy and might be cleared by filtering. Capt. Torrey saturated muslin in a chloroform solution of the asphalt and then exhausted the muslin strips with alcohol. He obtained a very viscous extract, but does not appear to have reached definite quantitative results.

In a series of experiments that the author carried on in California upon natural California asphalts and residuums from California petroleum, it was found that methyl, ethyl and amyl alcohols dissolved the constituents of asphalt in an increasing ratio and that the amount dissolved by either solvent varied with the temperature and the percentage strength of the alcohol. *The differences in the amounts dissolved varied so greatly under slightly changed conditions that all attempts to obtain quantitative results by the use of any variety of alcohol, as a solvent, were finally abandoned. The material dissolved out of the different natural asphalts and artificial residuums by either of the alcohols was in every case precipitated in red drops of very viscous fluid, whenever the alcoholic solutions were diluted with water. I am not aware that the composition of this red liquid has been investigated.‡

*Comptes Rendue, CXXIII, 1327-29; Chem. Zentralb., 1897, p. 399.

†Ann. Chem. Pharm., LVIII, 273; Chem. u. Tech. d. Nat. u. Kunst. Asphalte, p. 858.

‡D. Torrey, Physical Properties of Asphalts, Paving and Municipal Engineering, May, 1894; Sept., 1894.

S. F. Peckham, Jour. Frank. Inst., Mar., 1896.

Another neutral liquid that is closely allied to the alcohols and that may easily be obtained pure and dry is acetone—dimethyl ketone. I think its use as a reagent in the analysis of asphalt was first suggested by Dr. S. P. Sadtler. He objects to the method proposed by Miss Linton (page 154) as tedious, and describes the following method as a substitute:

"An asbestos filter is made in a weighed Gooch crucible and dried. About 10 gms. of fine white sand, previously ignited and cooled, are added, and a piece of stout platinum wire, about 3 in. long, is placed in the crucible and the whole dried to a constant weight at 100° C.

"Then 1 to 2 gms. of the asphalt, in fine powder, if a solid, are added, gently mixed with the upper portion of the sand layer with the aid of the platinum wire, care being taken not to disturb the asbestos filter below. The weight of the whole is accurately taken, inclusive of the wire and the crucible, and its contents then dried at 100° C. to a constant weight, either in an air bath or water oven, cooled in a desiccator and weighed. If the sample be a maltha (liquid bitumen), it is gently mixed with the sand layer, after slightly softening it with the aid of the drying oven. The loss at 100° C. is calculated and called 'moisture and loss at 100° C.' The crucible and its contents are then placed in a continuous extraction apparatus, formed by placing a small percolator within a larger one, the inner one being held in position by a perforated cork. The crucible having been placed in the inner percolator, the outer one is connected with a flask containing the solvent, and with an upright condenser. The flask is heated either on a sand bath or a water bath, the former being preferable, since when once regulated it needs no attention or renewal as does the water bath. The extraction with acetone, which is first undertaken, is continued until the loss on extracting for two hours is not more than 1 or 2 milligrams. The loss of weight after this extraction, as compared with the weight on starting the extraction is calculated and called 'petrolene.' The extraction is then continued in the same manner with chloroform, and the final loss is the 'total bitumen.' The time necessary to effect a thorough extraction varies greatly with the different asphalts, but it will not amount to more than twelve hours for the acetone and eight

hours for the chloroform extraction. The loss in weight should be taken first after four hours, and then every two hours until the extraction is complete, the crucible and contents being dried at 100° C., and cooled in a desiccator each time. The residue in the crucible then represents the organic non-bitumen and mineral matter. It is ignited, after placing the cap on the bottom of the crucible, and the loss calculated as 'organic non-bitumen', while the remainder is the 'mineral matter' or 'ash.' **

In a paper read before the Franklin Institute of Philadelphia, January, 1896, I showed that the solvent effects of acetone upon asphalts approached those of alcohols and were quite different from those of petroleum ether; for which reason acetone could not be substituted for petroleum ether in the analysis of asphalts, unless a new series of constants was established.

It was further shown in that paper that an acetone solution of Trinidad pitch, evaporated to dryness at about 60° C. yielded an organic residuum and deliquescent salt, which when dissolved away by water from the bituminous and very viscous residue, and evaporated to dryness, yielded an organic residue soluble in water. A portion of crude Trinidad pitch, exhausted with petroleum ether and chloroform, yielded to acetone a residue, a part of which was soluble in water, a part in sodium hydrate and a part in benzole. One gram of crude Trinidad pitch, after exhaustion in chloroform, yielded 1.59 per cent material soluble in acetone.

Equal portions of a very dry Egyptian asphaltum and an Athabasca River maltha, were exhausted with petroleum ether and with acetone, with the following results:

	Egyptian Asphaltum Percent.	Athabasca Maltha Percent.
Petroleum ether, soluble.....	38.03	73.86
Acetone, soluble.....	8.68	24.33

No difference was observed between the solvent powers of cold and boiling acetone in either case. The dry Egyptian asphaltum and the semi-fluid maltha exhibit the extremes to

*S. P. Sadtler, Jour. Frank. Inst., Nov., 1895.

which any solvent of bitumen is likely to be applied and the lack of parallelism is enormously large in both cases.

Later experiments upon Trinidad pitch have led to the conclusion that after exhaustion with water a clearly defined portion of the pitch is soluble in 95 per cent methyl alcohol. The solution is slowly accomplished and the amount of the soluble required to saturate the alcohol is comparatively small. So far as the soluble has been examined it is a reddish brown, semifluid body of great viscosity. It is readily acted on by a mixture of nitric and sulphuric acids, forming a nitro derivative of a deep red-orange color, heavier than water.*

After exhaustion with methyl alcohol a portion of the pitch many times larger is found to be soluble in pure dry acetone. This soluble is a very dense, slightly mobile, very viscous fluid, of a deep, cherry-red color. This body, too, will form a dense nitro compound with a mixture of nitric and sulphuric acids.

E. Jacobsen separated the soluble from the insoluble constituents of Syrian asphalt by the use of petroleum benzine (petroleum ether). He dissolves the asphalt in the least possible quantity of "coal tar benzol" (benzene), filters the solution and pours it into ten times the volume of petroleum benzine (sp. gr. 0.690 to 0.700). A precipitate is produced, which is gathered upon a filter and washed with petroleum ether (sp. gr. 0.650 to 0.660) until it passes colorless. The precipitate is weighed.†

Dr. Holde uses a method of precipitation. He shakes thoroughly 1.5 to 5.0 gms. of the bitumen in a 1-liter flask of colorless glass, with 300 to 500 c.cm. of benzine of the lowest possible boiling point, as the solubility of the asphalt decreases with the lowering of the boiling point. After standing at least a day, decant the larger part of the solution through a folded filter. Then bring the larger part of the precipitate upon the filter and rinse the flask with pure benzine until the filtrate no longer gives a residue upon evaporation. Dissolve the asphalt from the filter with pure hot benzole, then rinse the solution into a flask and distill off the larger part of the benzole, pour into a tared dish, evaporate the remainder of the

*Jour. Frank. Institute, March, 1896.

†Chem. Ind., 1879, p. 369.

benzole, dry at 100° C. and weigh. The solution of the asphalt from the filter must be made as soon as possible, in order to avoid any increase in weight from oxidation or absorption of hygroscopic moisture.*

Carl Engler has assumed that all crude petroleums contain paraffine, asphalt and pitch, which accumulate in the residuums from distillation. He assumes that maltha (Bergteer) and that which is related to natural asphalt (Erdpech) as produced from petroleum, include these principal constituents. Asphalt is that which is insoluble in the lightest Ligroin (the lightest distillate from petroleum—gasolene) and pitch is the part most easily soluble therein. At Engler's suggestion A. Flachs has worked out a method of separating these substances, which is based upon the process of Holde as well as upon an earlier research of Engler and Böhm. This research assumes that the original mixture, or a substance containing it, shall be dissolved in benzole and ether and the solution precipitated by alcohol. The pitch as well as the asphalt both dissolve in benzole and ether, and are both precipitated together by the alcohol. On filtering, the paraffine and oil in the solution may be determined by any known method. The precipitate may be extracted with Ligroin, of not more than 45° boiling point; the pitch passes into solution and may be determined by distilling off the solvent. The asphalt remains as a deep black insoluble powder.†

The same objections may be urged against the terms "asphalt" and "pitch" that have been urged against "petrolene" and "asphaltene." These "substances" as described are not identical in composition when obtained from different crude materials.

In 1894 Miss Laura A. Linton published a paper, which I quote entire.

"In the year 1837, J. B. Boussingault published his celebrated memoir on the "Composition of Bitumens." In the researches upon which this memoir was based he had discovered that certain bitumens yielded in one manner a portion of their content and in another manner another portion of their con-

*Lunge's Chem. Tech. Untersuchungs Methoden, 1905, III, p. 13.

†Zgl. Nachtrage uber den Bergteer von Pechelbronn; Inaugural dissertation, Basle, 1902; Lunge Chem.-Tech., 1905, III, 13.

stituent hydrocarbons. He called the first portion 'petrolene' and the second portion 'asphaltene.'*

"In 1827† Le Bel and Muntz went over the same ground and in 1883 Le Bel again went over it, adding a few facts in relation to other bitumens than those previously examined but leaving the two substances, petrolene and asphaltene, practically where he found them.‡

"In 1837 the conclusions based on chemical research were far less exact than at the present time and Boussingault concluded that the substances, petrolene and asphaltene, were simple substances and also that they were identical from whatever sources they were derived. In this conclusion Le Bel in a measure appears to coincide.

"It, however, requires no argument to prove, to any one at all familiar with the subject, that petrolene is nothing but a name that covers a great variety of substances, radically unlike, that exist in different forms of bitumen and are only related, in this instance, as being held in solution by a certain limited number of menstrua and which include the whole list of paraffines and iso-paraffines, the olefines, the benzines and additive benzines with many other less abundant and well-known substances.

"Ethyl ether and so-called petroleum naphtha, which latter is an indefinite mixture of fluid paraffines and iso-paraffines of high specific gravity, are the solvents used; but no determination has been made as to the influence of proportion in the mixtures of the substances dissolved, or as to the relative solvent powers of the two menstrua upon the different constituents of these mixtures. In fact petrolene is nothing but a name which at present covers a vast expanse of the unknown.

"It can be safely said that probability favors the assumption that asphaltene is a little more definite; but no certainty attaches to the identity of asphaltene from different sources or of asphaltene dissolved by different menstrua.

"Therefore, in a general way, it may be said that asphaltene is that portion of the different forms of bitumen that

**Annales de Chemie et de Physique*, lxiiv, 141.

†*Bull. Soc. Chem.*, 17, 156.

‡*Ibid*, 50, 359.

is soluble in carbon disulphide, chloroform, benzine and a few other less well-known liquids and is not soluble in the menstrua that dissolve petrolene.

"As the bitumens examined by the French chemists, above mentioned, have never assumed commercial importance, the questions relating to petrolene and asphaltene have remained matters of scientific interest only. However, since asphalt paving has become a business involving the expenditure of large sums of money these problems are beginning to assume a wide importance outside the laboratory of the chemist and to demand from technologists very serious consideration. Within recent years large numbers of so-called analyses have been reported, which represent various attempts to determine and set forth the relative value of many samples and kinds of asphaltum, that may or may not be suitable for the many uses to which asphaltum is applied, but more particularly with reference to street paving. Prominent among the chemists who have been more or less extensively engaged in these analyses of asphalts are Mr. Clifford Richardson, Dr. Henry Leffmann, Dr. Samuel P. Sadtler, and Dr. De Smedt.

"A perusal of the numerous published reports of Mr. Richardson reveals the fact that in his tests the solvents used for the extraction of petrolene and asphaltene, were petroleum ether and carbon disulphide, while Drs. Leffmann and Sadtler, in their investigations and tests of asphalts, used alcohol—presumably ethyl-alcohol—carbon disulphide, and ether as shown by the report submitted to the Citizens' Municipal Association and the Trades League of Philadelphia.

"Neither of these gentlemen describe any process or method employed in obtaining the results stated. It is hardly consistent with the nature of the reports that they should. Nor has Mr. Richardson, in an article published in the *Journal of Analytical and Applied Chemistry*, in the numbers for December, 1892, and January, 1893, given any detailed description of the process he employed in order to obtain the numerous results of analysis that he there uses.

"But little satisfaction can be derived from consulting

Allen's encyclopedic work so exhaustive upon every subject relating to technical organic analysis.*

"We find therein the following statements and notes concerning the solvents and methods used in the analysis of asphalts: 'For the determination of the total bituminous matters in asphalt rock and mixtures containing it, C. T. Kingzett extracts the air-dried sample with freshly distilled Russian oil of turpentine, evaporates (Analyst viii, 4) the resultant solution and weighs the residue. The matter insoluble in turpentine is washed with ether, the calcium and magnesium carbonates dissolved in hydrochloric acid and the washed insoluble siliceous matter weighed.'

"H. P. Cooper prefers carbon disulphide for dissolving out the bituminous matters from asphaltic mixtures.'

"Allen adds in a note, 'The carbon disulphide employed for dissolving the bituminous matter must not contain free sulphur. It may be replaced by chloroform or benzene (coal tar naphtha). If the residue left after extraction be dark colored, foreign organic matters of valueless nature are present. Their proportions may be determined by igniting the weighed residue left after dissolving out the asphaltum, recarbonating it with ammonium carbonate, again gently heating it and reweighing. The loss of weight is the amount of non-bituminous organic matter present. In the case of samples leaving a white residue after exhaustion with carbon disulphide, the bituminous matter may be simply and accurately ascertained from the loss on ignition, taking care to recarbonate the lime before weighing.'

"In another note, page 377, he says: 'Five grams of the finely divided sample were digested for one hour with fifty c.c. of petroleum spirit (sp. gr. 0.7) and the mixture frequently agitated. The liquid is then boiled for a short time, decanted and the residue boiled with another quantity of twenty-five cc. of petroleum spirit. This treatment is repeated eight or ten times until the exhaustion is complete.

"E. Davies (Pharm. Jour., [3], 14, p. 394), reports that none of the organic matter in Val de Travers asphalt is insoluble in petroleum spirit.'

*Commercial Organic Analysis, by Alfred H. Allen, London, 1886, 2, 375-7, and later editions.

"Now, when we take into consideration the fact that turpentine, carbon disulphide, ether, chloroform and benzine have been used indiscriminately by chemists in the extraction of asphaltene, the question very naturally arises, are the results that have been and that are being obtained by these different methods of analysis strictly comparable—that is, are they convertible terms? Will the same asphalt treated with different solvents show in each case the same percentage composition? If not, then it is evident that asphalt taken from different localities and subjected to dissimilar methods of analysis cannot yield results of any value so far as purposes of comparison are concerned. Then again, if turpentine, carbon disulphide, and chloroform give a different proportion of asphaltene in the same asphalt it is just as evident that asphaltene, instead of being a definite chemical substance, is a mixture, which mixture would doubtless vary in different asphalts.

"It was for the purpose of determining whether petroleum ether (paraffines), California naphtha, and ethyl ether are interchangeable solvents of petrolene and whether turpentine, carbon disulphide and chloroform are interchangeable solvents of asphaltene that the research, the results of which are here given, was undertaken. That a series of such tests, faithfully carried out, should lead to the establishment of a method of analysis applicable to all asphalts and, at the same time, reveal something regarding the real nature of petrolene and asphaltene was inevitable.

"The specimens analyzed were furnished me by Prof. S. F. Peckham, Chemist of the Union Oil Co. of California, and were as follows:

"(1) **Crude Trinidad Asphaltum.**—From the Warren-Scharf Asphalt Co., of New York City. This specimen contained little or no water, as, for several months, it had been broken in small pieces, and so had lost the water which this asphaltum generally contains.

"(2) **Cuban Asphalt.**—A commercial sample obtained in New York City.

"(3) **Kuban Residuum.**—An artificial asphalt obtained from the distillation of Kuban petroleum from the western extremity of the Caucasus Mountains, Russia.

"(4) **Egyptian Asphalt.**—An Assyrian asphalt taken from the Dead Sea and imported into Egypt. This specimen was obtained in New York City.

"(5) **Asphaltic Rock.**—From Val de Travers, Switzerland. This asphalt was a sample of natural rock obtained at the office of Wm. H. Delano, representative of the French Company in New York City.

"(6) **Seyssel Asphaltic Rock.**—From the well-known locality in eastern France, obtained from the same source as No. 5.

"(7) **Turrellite.**—From a deposit lately discovered in Uvalde County, Texas, consisting of a mass of sea-shells cemented together by bitumen into a solid rock mass. It occurs in a rock formation said to be of Jurassic age, in which formation the Val de Travers rock also occurs. This specimen was obtained from the office of the Litho-carbon Co. of New York City.

"(8) **Kentucky Asphaltic Rock.**—Obtained from Marshall Morris, Louisville, Ky.

"(9) **An Asphaltic Mineral.**—Resembling Gilsonite; reported as coming from Utah.

"(10) **California Maltha.**—Taken from a well at Summerland, on the coast, near Santa Barbara.

"(11) **Asphaltum.**—From mines recently opened near Asphalto, Kern County, California, in the eastern foothills of the Coast Range Mountains, about thirty miles west of Bakersfield.

"(12) **Asphaltic Sandstone.**—From San Luis Obispo, Cal.

"(13) **Asphaltum.**—Picked up on the beach at San Buena Ventura, Cal., washed in from the Santa Barbara channel.

"(14) **Asphaltum.**—From the Ojai ranch, Ventura Co., Cal.

"(15) **Grahamite.**—A so-called asphaltum taken from a vein in Ritchie Co., W. Va.

"(16) A portion of a compressed brick made from the asphaltic rock taken from the Seyssel mines. Exhibited at the Columbian Exposition.

"(17) **Hard Artificial Asphalt.**—An asphaltic residue obtained from the distillation of petroleum obtained near Santa Paula, Cal. It is known in the refinery of the Union Oil Co., of California, as grade "B."

"(18) **Soft Artificial Asphalt.**—From the refinery of the Union Oil Co., of California, at Santa Paula. Grade "D."

"(19) **Asphaltic Pavement.**—Obtained from Franklin avenue, Buffalo, N. Y. It was laid in 1878, of Trinidad asphalt, wax tailings, and very fine sand. It is remarkable as having been laid for 15 years with almost no need of repairs.

"(20) **Asphaltic Pavement.**—From Governor's Island, New York Harbor, laid within the fort at an unknown date, but so old that it has begun to break up from natural causes. Obtained from J. A. W. Pine, of New York City.

"(21) **Dubb's Artificial Asphalt.**—A so-called asphaltum obtained in operating the Dubb's patent process for the manufacture of asphaltum by adding sulphur to hot Lima-tar and thereby burning out the hydrogen. This is an asphalt only in name. The specimen was obtained from J. A. W. Pine, of New York City.

"(22) **Roofing Pitch.**—Obtained from Mica-asphalt Co., of New York City.

"(23) **Pitch.**—Obtained as a residuum in the distillation of Scotch blast-furnace tar. This specimen was obtained from the same source as Nos. 20 and 21.

"In making tests to determine the best methods to be used in the analysis of asphalts the well known Trinidad and Cuban asphalts were used and all analyses were made in duplicate. In the case of asphalts rich in bituminous matter about a half gram of the material, finely powdered, was used but in the case of asphalts in which the mineral matter constituted a large proportion the quantity was increased to several grams.

"The sample was weighed in an Erlenmeyer flask and digested over night in about fifty c. c. of petroleum ether; in the morning the clear solution, containing the dissolved petrolene, was passed through a balanced filter and a fresh portion of petroleum ether added to the contents of the flask. The second digestion was continued for two or three hours

when the solution, as before, was filtered off and the process repeated until the whole of the petroleum had been removed. The contents of the flask were then thrown upon the filter and thoroughly washed with petroleum ether. Cold turpentine was then poured upon the filter in successive portions until the filtrate passed through colorless when the assumption was made that all the asphaltene and consequently all the bituminous matter had been removed.

"The remaining organic matter, not bituminous, was determined by difference, that is, the residue on the filter, after digestion in turpentine, was washed with ethyl alcohol, dried, and weighed in order to determine the percentage of asphaltene after which the residue was burned in a platinum crucible, the difference in weight representing the organic matter not bituminous.

"The contents of the crucible were now purely inorganic and, in the case of most asphalts, the residuum was sand more or less colored with iron.

"The analysis of Trinidad asphalt under this treatment gave so low a percentage of asphaltene and so large a proportion of organic matter not bitumen, that it was clearly evident that cold turpentine had not dissolved, and could not dissolve all of the asphaltene.

"A second set of experiments was then tried in which cold turpentine and carbon disulphide were used as solvents of asphaltene. The results obtained for samples 1 and 2 were as follows:

Sample.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
No. 1	32.54	20.3435	12.368	34.6775	99.929
No. 2.... ..	25.049	54.53	2.441	17.9215	99.9415

"The experiment was now made of somewhat varying the method of treatment for the following reasons: First, because of the difficulty of dissolving out the asphaltene while on the filter by simply allowing the solvent to run through it, and secondly, because, in consequence of the high specific gravity of petroleum ether, a considerable portion of sand or other mineral matter, mixed with asphaltene, always adhered to the flask, thus necessitating a separate determination of this portion. The method now employed for the removal of

petrolene and asphaltene was the decantation method, and the solvents used for asphaltene were hot turpentine and chloroform.

"The samples were digested over night in petroleum ether; in the morning the solution containing the petrolene was, as far as practicable, removed from the flask and the remainder was evaporated over a steam-bath; after weighing, the residuum containing the asphaltene was digested in hot turpentine over the steam-bath, and finally, the whole contents of the flask were poured upon a balanced filter and treated as in the first experiments.

"The percentage composition of Nos. 1, 2, and 17, as determined by the decantation method, was as follows:

Sample.	Petrolene.	Asphaltene.	Other organic		Total.
			matter.	matter.	
No. 1	31.51	22.9865	11.4195	34.073	99.989
No. 2	25.055	52.245	5.758	16.918	99.962
No. 17	64.571	21.2545	13.706	0.3613	99.8928

"In carrying out this method a great many determinations were lost, due to the fact that, in evaporation to dryness over the steam-bath, the contents of the flask were in part bumped out. In consequence, this method was soon abandoned as impracticable, and finally, funnels with stop-cocks were employed, in which the contents of the filter could be digested. Boiling hot instead of cold turpentine was used, and, when necessary, the digestion was continued over night, and all the after washings were made with hot turpentine. Numerous trials showed that carbon disulphide dissolves little more than hot turpentine. The last trace of asphaltene, insoluble in either turpentine or carbon disulphide, was removed by chloroform.

"In order to determine the relative solvent power of hot turpentine, carbon disulphide, and chloroform, the following method of qualitative analysis was applied to the twenty-three samples enumerated above. From a half gram to one gram of the material was digested over night in a four-ounce Erlenmeyer flask with about fifty c. c. of petroleum ether. Next morning the contents of the flask were poured upon a filter, and the undissolved residue washed with petroleum ether until the filtrate was no longer colored. Boiling spirits of

turpentine was then poured upon the filter until it passed through colorless, when carbon disulphide was used in the same manner, followed lastly by chloroform. The action of the successive solvents is shown in the following table:

Sample. No.	Hot turpentine.	Carbon disulphide.	Chloroform.
No. 1.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
No. 2.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a perceptible amount.
No. 3.	Dissolves nearly all.	Dissolves a trace.	Dissolves a trace.
No. 4.	Dissolves nearly all.	Dissolves the slightest trace.	Dissolves the slightest trace.
No. 5.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
No. 6.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
No. 7.	Dissolves nearly all.	Dissolves the slightest trace.	Dissolves the slightest trace.
No. 8.	Dissolves nearly all.	Dissolves the slightest trace.	Dissolves a trace.
No. 9.	Dissolves nothing.	Dissolves nothing.	Dissolves a trace.
No. 10.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
No. 11.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
No. 12.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
No. 13.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
No. 14.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
No. 15.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.
No. 16.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
No. 17.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.
No. 18.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.
No. 19.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
No. 20.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
No. 21.	Dissolves nearly all.	Dissolves a trace.	Dissolves a trace.
No. 22.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a trace.
No. 23.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.

"Of the twenty-three asphalts examined, there was not one that did not yield some asphaltene on treatment with chloroform; consequently, it is safe to infer that in the analysis of asphalts, unless final washing be made with chloroform, the per cent of asphaltene will be too low. There was

a marked difference observed in the different asphalts as to the manner in which their constituent asphaltene was dissolved on treatment with hot turpentine. In Nos. 4, 5, 6, and 7, and a few others, the asphaltene dissolved out in a few minutes, while in the case of others, notably No. 15, it was a matter of hours, and even of days, before every trace soluble in turpentine could be removed. No. 9 seems to be an asphaltic freak as it contains no petroleum whatever and is insoluble in both hot turpentine and carbon disulphide, while chloroform and amyl alcohol dissolve but the slightest trace.

"It was a difficult matter to determine the relative quantity of asphaltene dissolved by the different menstrua, as the only guide used was the color of the filtrate. This suggests a most interesting research—the fractional, quantitative determination of asphaltene.

"From my experience in the analysis of asphalts, I would advise that a preliminary qualitative analysis be always made of each new variety of asphaltum before any quantitative determinations are attempted, care being taken to observe the behavior of different asphalts with the different solvents. This method of procedure is to be recommended, not only because it would prove an economy of time and reagents used, but also because, in this way, much would be learned concerning the nature of petroleum and asphaltene.

"A trial was made with Cuban asphalt to determine the solvent power of petroleum ether (87° Beaumé) as compared with that of California naphtha (74° Beaumé) and ethyl ether with the following results:

Sample.	Solvent for petroleum.	Per cent of petroleum.
No. 2.	Petroleum ether	25.8516
No. 2.	California naphtha	32.444
No. 2.	Ethyl ether	32.5455

"The high percentage of petroleum when California naphtha or ethyl ether are used indicates that the asphaltene is, in part, dissolved, and consequently, that these menstrua cannot be used as solvents of petroleum in the determination of asphalts.

"In selecting a method for the quantitative analysis based upon the results of these experiments, it is assumed that, until

a strictly scientific method is worked out, the present empirical determination of petroleum and asphaltene will continue in use. The three considerations of economy, speed, and convenience, will together control the selection. So long as the significance of the difference between the 25.8 per cent dissolved by petroleum ether and the 32.5 per cent dissolved by ethyl ether is an unknown element in the problem—that is, whether it be seven per cent of petroleum or of asphaltene that is involved—it is better to use petroleum ether, because it is cheap and easily obtained of a uniform quality. So, too, it is better to use boiling hot turpentine followed by chloroform as solvents of asphaltene, and thus rid ourselves of carbon disulphide altogether.

“With these considerations in view the following method of analysis is recommended:

“Weigh two suitable portions in four-ounce Erlenmeyer flasks, add fifty c. c. of petroleum ether, cover, and allow to stand over night. The following morning decant the liquid upon a balanced filter placed within a three-inch funnel provided with a stop-cock in the neck. Add another portion of petroleum ether to the flask, allowing two or three hours for digestion, and decant the liquid upon the same filter as before; this process is to be continued until the liquid ceases to be colored, then transfer the whole of the bitumen to the filter. Dry the flask in a steam-bath and weigh; any increase in weight of the flask should be subtracted from the amount determined as petroleum. Wash the filter and its contents with petroleum ether, place these with the filter counterpoise in a steam-bath, dry, and weigh; the loss in weight of the bitumen represents the petroleum.

“Rinse the flask thoroughly with boiling turpentine and add the liquid to the filter in the closed funnel, pour upon the filter a sufficient quantity of boiling turpentine to wholly submerge it, cover and allow the digestion to continue for several hours or over night. Repeat the digesting and filtering with boiling turpentine until the filtrate becomes colorless. The filter should be much smaller than the funnel. Rinse the flask with chloroform and pour upon the filter, add sufficient chloroform to wholly submerge the filter and allow at

least an hour for digestion; wash with chloroform until the filtrate passes through colorless, then dry and weigh; the loss in weight represents the asphaltene. The filter is now to be burned in a platinum crucible and, if the asphaltum be combined with limestone, the residue recarbonated with ammonium carbonate, dried in a steam-bath, and weighed, the loss in weight represents the organic matter not bitumen, or coke, in the case of artificial asphaltic residuum, produced by heat.

"There is necessity for washing the flask with the different solvents, not only because the petroleum ether is too light to rinse out all of the mineral matter, but also because some of the asphaltene adheres to the flask. Generally the turpentine removes all of the mineral matter, as well as part of the asphaltene, but if it does not, then after the flask is rinsed with chloroform it must be again dried and weighed and the increase in weight added to the weight of the mineral matter in the platinum crucible. If water be present the asphalt should be dried in a steam-bath to a constant weight before being digested in petroleum ether. It is possible that some natural asphalts might experience a trifling loss of volatile oils at the temperature of the steam-bath, but in most instances such loss would be too slight to be regarded. With care and patience this method has been found capable of yielding very closely concordant duplicate results at each step.

"The following table exhibits the results of a number of quantitative analyses made according to this method:

Sample.	Water.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total
No. 1 ..	2.029	32.4455	22.1115	8.1215	35.2865	99.994
No. 2 ..	0.3911	25.4605	54.414	2.469	17.0305	99.7651
No. 4	35.087	63.183	1.7285	99.9985
Not recarbonated.						
No. 5	8.518	3.924	25.791	61.764	99.997
No. 6	7.486	4.316	88.198	100.
No. 7	8.786	3.267	87.947	100.
No. 8	3.349	2.4215	94.228	99.9985
No. 12 ..	0.335	11.323	3.81	1.124	83.407	99.999
No. 15	49.959	50.041	100.
No. 17	64.571	21.2545	13.706	0.3613	99.8928
No. 18	63.498	29.966	6.095	99.559
No. 19	4.387	2.831	4.102	88.65	99.97
No. 20 ..	0.434	6.666	1.87	3.697	87.33	99.997
No. 21	66.788	31.932	1.278	99.998

"While this research is in no sense complete—it has in fact but opened up a wide field for further work—yet, sufficient evidence has been obtained to show that petrolene and asphaltene are not substances, but empirical terms that designate mixtures of substances soluble under certain conditions in different menstrua.

"It is not unfair to assume that in these empirical mixtures, so long known under the names of petrolene and asphaltene, the lower members of all the different groups of hydrocarbons now known may be found. Again—just as some petroleums, which are varieties of bitumen, consist chiefly of paraffines—notably Pennsylvania petroleum—and some, like Russian petroleum, consist of the additive benzines, while still others contain mixtures of the two, is it not reasonable to presume that solid bitumens, like liquid bitumens, are equally variable in composition? If this be the case, then it is equally fair to assume that any solvent taken will not dissolve substances of identical composition from different asphalts.

"A review of the results here given suggests the query, have the methods heretofore employed for the technical analysis of asphaltum really been analytical at all? Would not a method and process suggested by the results of the qualitative analyses given in this paper and based on the successive application of different solvents and yielding results similar to those of fractional distillation really become analytical, especially if the separate portions dissolved by the different solvents were subjected to such treatment by oxidizing agents as would enable us by a comparison of the products of oxidation to determine to what groups of hydrocarbons the different substances dissolved respectively belong?

"I take pleasure in hereby acknowledging my indebtedness to the courtesy of Hon. Thos. R. Bard, President of the Union Oil Co., of California, for the use of the laboratory of the company while engaged in this research.*

In March, 1896, Miss Linton published a second paper, from which I quote as follows:

*Laura A. Linton, S. B., M. D.; Journal of the American Chemical Society, Vol. XVI, Dec., 1894.

"The method universally employed for the determination of the incorporated water of asphaltum is that of estimating the loss in weight of the substance when exposed to a temperature of 100° C. The possibility of a loss of more or less of the inherent volatile matter when heated to such a high temperature must have occurred to every one engaged in the analysis of asphaltum. A series of experiments made during the past few months has confirmed my suspicion that such is the case.

"The experiment proper consisted in heating a weighed portion of asphaltum in a combustion tube, the general arrangement of the apparatus being the same as that employed in the determination of water in organic analysis. The temperature was gradually raised from the temperature of the room to that of boiling water. The tube was swept out before and after heating with either dried air or dried hydrogen. Simultaneously with this experiment two other weighed portions of the same asphaltum were dried, one in an oven at 100° C. to serve as a check upon that portion dried in the combustion tube, while the other portion was dried in the sun.

"As the method of sun drying requires several days it was done in a room as free as possible from dust and, to increase the temperature and at the same time to exclude all foreign matter, the samples were placed in large watch glasses with watch-glass covers fitting loosely to allow of circulation of air. In this lens-like arrangement the maximum temperature did not exceed 50° C. On cloudy days the drying was necessarily done in the oven below 50° C.

"These experiments showed that the asphaltum tested did not oxidize below 100° C., as aspiration with dried air and dried hydrogen give the same results; and also that all moisture is driven off below 50° C., while between 50° C. and 100° C. a certain portion of oily matter is lost, this oil invariably collecting in drops about the mouth of the combustion tube. In the light of these facts it becomes clear that the old method of determining moisture, if it is to be determined at all, is incorrect since the percentage lost on heating the asphaltum to 100° C. includes not only the water but also that part of the petroleum volatile below 100° C.

"The moisture associated with an asphaltum being hygroscopic, as is evident from the fact that the same specimen carries a constantly varying proportion depending on atmospheric conditions, it should never be estimated as a constituent part of the asphaltum, particularly in making analyses for purposes of comparison.

"In making all of my recent analyses, as a preliminary, I have air-dried to a constant weight several grams of the sample to be analyzed before weighing out the portion to be treated with the different solvents, thus entirely excluding water from the percentage composition of the asphaltum.

"A second departure from the method previously given is a purely mechanical one. As a matter of convenience I have discarded the use of the Erlenmeyer flask, the substance being weighed out on balanced filter-papers instead. In this way all digestion is done in separatory funnels. This method of treatment is very simple and the results obtained are good, but care must be taken that the solution in the funnels does not become too concentrated before running off through the tap, otherwise the petroleum precipitates itself, more or less of it adhering to the outside of the filter-paper. To prevent this the petroleum ether may be drawn off every few minutes until the greater part of the petroleum has been extracted, after which it is perfectly safe to allow the digestion to continue for hours in removing the final traces.

"Lastly, I have obtained some interesting and, in my opinion, important results by fractionating the asphaltene, determining it in two portions: that soluble in boiling turpentine and that soluble only in chloroform. The process is a very tedious one on account of the difficulty of removing the very last trace soluble in boiling turpentine, but the results that follow are a sufficient warrant for the expenditure of so much time, which, for the specimens analyzed, ranged from one to four weeks. In order to secure concordant results in duplicate analyses I found it necessary to pursue the following course:

"After the removal of the petroleum the residue on the filter was digested in boiling turpentine until the filtrate was colorless, when the contents of the filter were washed in alco-

hol and dried at 100° C. If, on drying, a black, semi-liquid substance separated from the mass, this was an indication that the turpentine fraction had not been entirely removed, in which case the process was repeated. In the most refractory specimens this treatment was applied many times. The tardy yielding to the solvent power of the turpentine is doubtless largely due to the fact that the turpentine does not readily penetrate the mass and it may be, also, that the chloroform fraction prevents the action of the turpentine just as gold protects silver from the action of nitric acid. The completion of the process is always indicated by the appearance of the dried residue which, after the complete removal of the turpentine fraction, is invariably a loose, brown powder without coherence. This treatment shows that part of the asphaltene soluble in boiling turpentine to be a black, viscous, semi-liquid substance resembling tar and having a melting point at or below 100° C.

"Another fact, which may prove valuable as well as interesting, is clearly brought out in this fractionation of asphaltene and that is that not only do the 'aged' varieties of asphaltum contain a larger percentage of asphaltene but the turpentine fraction becomes a smaller proportion of the total bitumen while the chloroform fraction becomes larger.

"An investigation of the table of the percentage composition of the following varieties of asphaltum will confirm this statement:

"(1) An average sample of land asphaltum from the island of Trinidad.

"(2) Altered or 'aged' (iron pitch) Trinidad land asphaltum.

"(3) Altered or 'aged' Trinidad land asphaltum.

"(4) An average sample of Trinidad lake asphaltum.

"(5) An altered or 'aged' Trinidad lake asphaltum.

"(6) An altered or 'aged' Trinidad lake asphaltum.

"(7) An altered or 'aged' (iron pitch) Trinidad lake asphaltum.

"(8) Asphaltum from Montague Co., Texas.

"(9) Turrellite from Uvalde Co., Texas.

"(10) Asphaltum from near Ardmore, Oklahoma.

"(11) Grahamite from Ritchie Co., W. Va.

"(12) Seyssel asphaltic rock from eastern France.

Sam- ple.	Petrolene.	Turpen- tine fraction.	Chloroform fraction.	Asphal- tene.	Total bitumen.	Ratio of chloroform to matter		Mineral matter.
						total bitumen.	not bitumen.	
1.....	33.73	15.67	3.179	18.849	52.579	1:16	11.528	35.886
2.....	33.574	13.7	9.627	23.327	56.901	1:6	8.414	34.684
3.....	21.362	15.2	15.112	30.312	51.674	1:3	9.85	38.375
4.....	35.40	12.300	5.287	17.587	52.987	1:10	10.962	36.100
5.....	26.925	18.613	6.687	25.3	52.225	1:8	11.237	36.537
6.....	19.25	22.35	10.962	33.312	52.562	1:5	9.562	37.875
7.....	22.25	9.785	12.54	22.325	44.575	1:4	8.937	46.462
8.....	7.538	1.601	trace	1.601	9.139	90.861
9.....	8.786	3.267	trace	3.267	12.053	87.947
10.....	9.503	0.9905	trace	0.9905	10.4935	89.5065
11.....	49.959	17.458	82.583	50.041	100.00	1:3
12.....	7.486	3.945	0.371	4.316	11.802	1:31	88.198

"I am not yet prepared to say that the turpentine fractionation of asphaltene, if made in the case of the asphaltum obtainable from different parts of the world would indicate the relative 'aging' of the different varieties, but my experience with Trinidad pitch inclines me to think that this will prove the case when such analyses are made."*

In Vol. III, 1903, of the Proceedings of the American Society for Testing Materials, A. W. Dow, of Washington, D. C., describes a process for "Testing Bitumens for Paving Purposes," as follows:

"Chemical Tests.—There has been but little done that is of practical value in chemical tests on bitumens, and there is so much confusion in what has been done that it is difficult for any one without considerable experience and knowledge of the subject to distinguish what is of practical value. One source of confusion in the examination of asphalts by chemical means results from the careless statement of methods of analysis given in some of our standard textbooks. An example of this is found in Sadtler's 'Hand Book of Industrial Organic Chemistry,' page 42. He states:

"When on the other hand the asphalt is to be considered with reference to its value for asphalt paving purposes, it is necessary to examine into the quality of the bitumen. For

*Jour. Am. Chem. Soc., xviii, Mar., 1896.

this purpose the total bitumen (amount soluble in carbon disulphide), organic not bitumen, and ash are first determined. Then the amount soluble in petroleum naphtha (so-called petrolene) is ascertained. The difference between this and the total bitumen is called asphaltene. * * * Instead of petroleum naphtha and carbon disulphide, acetone and chloroform may be used with advantage for extractions.' While there is but slight difference between the results obtained from carbon disulphide and those obtained by chloroform extraction, yet there is no similarity at all in the solvent power of acetone and petroleum naphtha, and for this reason the results are not comparable. By the exercise of a little care in the compiling of such books a great benefit would result to those who have not the time to go deeply into the subject.

"An illustration of the confusion resulting from the introduction of acetone as a solvent is found in the second edition of Stillman's Engineering Chemistry, page 438. He here gives a method of analysis by which the asphalt is first extracted with acetone, and then by chloroform as recommended by Sadtler, and calls the material extracted with the acetone petrolene. He then goes on to give the method of L. A. Linton (J. A. C. S. 18, 375), in which the asphalt is first extracted by petroleum ether, then turpentine, and afterward with chloroform. He here speaks of the bitumen that has been extracted with petroleum ether as petrolene. If the bitumen soluble in petroleum ether is to be called petrolene, surely the same author should not make the mistake and call a totally different set of hydrocarbons, that are dissolved out by acetone by the same name. There is yet another class of bodies derived from asphalt that are known by the name of petrolene. In 1837 Boussingault subjected an asphalt to the process of distillation, naming the liquid that distilled off petrolene, and the residue left in the retort asphaltene. Dr. H. Endemann subjects asphalts to the Boussingault process, applying his terms to the distillate and residue which he obtains. Here are three distinct methods of separation applied to asphalts, each separation producing totally different complex compounds, yet the same terms, petrolene and asphaltene, are applied to the products obtained in each separation.

This leads to so much ambiguity in the subject that I can see no way to right things but by the abandonment of the names petrolene and asphaltene. I would advise the use of the terms naphtha soluble, acetone soluble, etc., for the products extracted with these solvents.

"Still another error into which people are led by some literature on the subject when they first take up the study of asphalt is the belief that petrolene and asphaltene are each a definite chemical compound. The petrolene and asphaltene obtained in any of the processes mentioned are not simply compounds, but complex mixtures of many chemical compounds, and petrolenes and asphaltenes derived from different asphalts are totally different from each other in their composition, and for this reason such determinations on asphalts can bear no relation whatever to their physical properties or suitability for paving. I cannot too highly recommend to all who are confused about the nomenclature and analysis of asphalts that they read the excellent chapter in the Bulletin of the University of Texas, No. 15 ('Coal, Lignite and Asphalt Rocks'), by Henry W. Harper. He discusses most comprehensively the ambiguity of the method and nomenclature of this subject. His results on the bromine absorption applied to different so-called petroleums and asphaltenes are evidence sufficient that these complex compounds differ in composition in every asphalt.

"Bitumen Soluble in Carbon Disulphide.—It is usually considered that all the cementing material of an asphaltic cement is soluble in carbon disulphide, but there is good ground for the belief that this is only approximately true and that the carbon disulphide in some cases dissolves materials that play no more part in the cementing than so much sand, while in others it leaves part of the cementing material undissolved. As, however, we have no means at the present time of determining the absolute quantity of cementing material in an asphaltic cement, and as the quantity soluble in carbon disulphide is as close an approximation as any, and this solvent is more generally used than any other, I advise adhering to its use. It is for this reason that the use of chloroform or turpentine, as advised by some analysts, because it dissolves a

little more from asphalt than does carbon disulphide, is not only unnecessary, but not advisable. There are numerous methods applied to the extraction of asphalt with carbon disulphide, the important ones of which can be found in Allen's Commercial Organic Analysis, Vol. II, Part II. Most of these methods are based on separating the insoluble from the soluble matter by filtration, and no correction is made for finely divided material, other than bitumen, which passes through the filter. From investigation I find that more or less finely divided mineral matter and organic matter not bitumen passes through the filter. It is claimed by some that this mineral matter is all in chemical combination with bitumen, but I often find in the examination of paving mixtures that the finely ground limestone which is used in the mixture is found in the filtrate. I also find that the filtrate from some asphalts invariably contains finely divided organic matter which will subside on standing. It is seen from the above that for a method to be the most accurate, filtration cannot be depended on, for even though the filtrate be evaporated off and burned, in which a correction for the mineral residue passing the filter is made, the insoluble organic matter which has passed the filter is burned off and considered as bitumen. It is for this reason that a method in which a long subsidence is used is the most preferable. The following is a method which I find, from long experience, gives the most accurate results: The asphalt, or like substance, is spread in a thin layer in a suitable dish (nickel or iron will do) and kept at a temperature of 225° F. until it practically stops losing in weight. The greater part and in some cases all the water and some light oils are expelled in this way. From 2 to 10 gms. (depending on its richness in bitumen) of this substance is weighed in a large-sized test-tube (8 ins. long by 1 in. in diameter), the tare of which has been previously ascertained. The tube containing the substance is then filled to within 1½ ins. of the top with carbon disulphide and allowed to stand for a few minutes. Then the tube is tightly corked with a good sound cork. It is then shaken vigorously until no asphalt can be seen adhering to the bottom. Care should be taken when shaking to keep one finger on the cork to prevent its

being blown out. The tube should then be put away, still corked, in an upright position, and not disturbed in the slightest way for two days, after which the carbon disulphide is decanted off into a second tared tube. As much of the solvent should be poured off as is possible without losing any of the residue. The first tube is again filled with fresh carbon disulphide and shaken as before and put away for two more days. The second tube is also corked and put away in an upright position. At the end of two days the contents of these two tubes are decanted off onto a weighed Gooch crucible fitted with an asbestos filter, the contents of the second tube being passed through the filter first. The residue in the second tube is then treated with about 2 c.c. of carbon disulphide, care being exercised to disturb it as little as possible, the treatment being to remove the small portion of solvent containing bitumen. The Gooch crucible is then washed with clean carbon disulphide until the filtrate is colorless. The crucible and the two tubes are then dried at 225° F. and weighed. The filtrate containing the bitumen is evaporated, the bituminous residue burned, and the weight of the ash added to that left in the two tubes and the Gooch crucible. The sum of these weights deducted from the weight of the substance taken gives the weight of the bitumen extracted.

"The practice of some analysts to first extract the bitumen soluble in naphtha or other solvent, and then extract the remaining bitumen with carbon disulphide, is not safe with some asphalts, as some of the residual bitumen is apt to be rendered insoluble, possibly by oxidation while driving out the first solvent.

"Bitumen Soluble in Naphtha.—The amount of bitumen soluble in naphtha, as has been before explained, is of no value excepting as generally indicating within broad limits the degree of hardness of an asphalt. The only advantage of this test is that it requires no other apparatus than is found in every chemical laboratory, and if standard methods could be adopted for its use, making a determination for the bromine absorbed on the naphtha-soluble bitumen and the bitumen insoluble in naphtha, the test might be made of interest in the examination of asphalts. The statement often made

that an asphalt which contains more than 30 per cent of asphaltene (bitumen insoluble in naphtha) is unsuitable for paving is not founded on facts. It does not matter how much asphaltene an asphalt contains so long as it can be softened into a proper cement by the addition of a suitable flux. I have, myself, seen asphalt which contained over 50 per cent of asphaltene made into paving cements, and excellent pavements made therewith. It is also occasionally seen stated that the suitability of an asphalt cement for paving can be determined by estimating the petrolene which it contains. This has been denied by Prof. Peckham, who insists 'that the bitumen of Trinidad pitch consists of asphaltene dissolved in petrolene, and that its cementitiousness is just as much due to one as to the other. Sand cannot be cemented with either petrolene or asphaltene alone, neither can wood be cemented with either water or glue alone. The cementitiousness depends upon the amount and quality of the bitumen present.' I agree heartily with this remark of Prof. Peckham in all respects but one, and that is: I would say that an asphalt consists of asphaltene in a more or less perfect solution of petrolene, as I find that in nearly all cases that while a portion of the asphaltene is evidently in solution in the petrolene there is another portion that exists in what might be called a colloidal solution.

"I have adopted the following method for the determination of the bitumen soluble in naphtha: A quantity of the asphaltic material sufficient to contain about 1 gm. of bitumen is weighed into a 3-oz. Erlenmeyer flask. This is treated with 50 c.c. of naphtha. The flask is then corked and shaken several times during the first two or three hours, when it is placed away for twenty-four hours. The solution is then carefully decanted onto a weighed Gooch crucible with an asbestos filter. This decanting can be done very close, and it does not matter if some of the residue does flow into the crucible. The residue is then treated with consecutive portions of naphtha until the filtrate becomes practically colorless. The sum of the weights of the residue in the flask and in the crucible is deducted from the weight of the substance taken, and gives the amount of the bitumen soluble in the naphtha.

"As the solvent power of different naphthas varies, it is very essential that the same naphtha be used each time for making this determination, and it is also necessary to make the extraction at the same temperature each time, as the higher the temperature the more solvent action is exerted by the naphtha. It is for this reason that I do not advise the use of the Soxhlet or other forms of extraction apparatus that use return condensers, as it is next to impossible to have the extracting solvent at the same temperature for each extraction. If the extracting is done by the method which I have described, the naphtha will be of the temperature of the laboratory, which is usually quite constant. The naphtha which I use for extracting distills between 60° and 80° F., and has a specific gravity at 60° F., closely approximating 0.680."*

Mr. Clifford Richardson has given in his "Modern Asphalt Pavement," Ed. 1905, the following data under Methods of Analysis:

"Determination of Total Bitumen.—One gram of the dried or refined material, in a state of very fine powder, if possible, is weighed out and introduced into a 200 c.c. Erlenmeyer flask of Jena glass and covered with about 100 c.c. of bisulphide of carbon. It is then set aside for at least five hours, or overnight, at the temperature of the laboratory. In the meantime a Gooch crucible is prepared with an asbestos felt and weighed. This Gooch crucible is of special form, with a large filtering surface. It holds 30 c.c., is of 4.4 cm. wide at the top, tapering to 3.6 cm. at the bottom and 2.6 cm. deep. This is much better for percolation work than the usual narrow form of Gooch. The felt is made by beating up long-fiber Italian asbestos in a mortar, and suspending the finer particles in water and quickly pouring off from the coarse particles. Too much of the latter should not be removed, or the felt will be too dense. The decanted asbestos and water can be kept in a bottle for use. To prepare the felt the asbestos and water are shaken up and what is found to be a proper amount poured into the crucible, which has in the meantime been attached to a vacuum filtering-flask by the proper connections. As soon as the asbestos has somewhat

*Proc. Am. Soc. for Testing Materials, III, p. 362, 1903.

settled the vacuum-pump is started and the felt firmly drawn on the bottom of the crucible. It is then dried, ignited and weighed.

"After standing a proper time the bisulphide is decanted very carefully upon the filter, which is supported in the neck of a wide-mouthed flask and allowed to run through without pressure. The flask, after being tipped to pour the first portion, is not again erect, in order to avoid stirring up the insoluble material, but is held at an angle on any suitable base, such as a clay chimney. After all the bisulphide has been decanted more is added, and the insoluble matter shaken up with it. This is allowed to settle and decanted as before, the insoluble matter being finally brought on the filter and washed with the solvent until clean. The excess of bisulphide is allowed to evaporate from the Gooch crucible at the temperature of the room. It is then dried for a short time at 100° C. and weighed. The loss of weight is the percentage of bitumen soluble in CS_2 .

"In the meantime, however, the bisulphide which has passed the filter is allowed to subside for twenty-four hours, if possible, and is then decanted carefully from the flask in which it has been removed, into a weighed platinum or unweighed porcelain dish. If there is any sediment in this flask it must be rinsed back into the Gooch crucible with bisulphide and the crucible again washed clean. The solvent in the dish is placed in a good draught and lighted. When all the bisulphide has burned the bitumen remaining in the dish is burned off over a lamp and the mineral residue, which is too fine to subside, is weighed if the burning is done in a platinum dish, or dusted out and added to the crucible if in a porcelain one. In the former case the weight is added to that of the Gooch crucible or subtracted from the per cent of bitumen, found without its consideration, as a correction. Care must be used in this method of procedure that the solvent does not creep over the sides of the crucible and that the outside is free from bitumen before weighing. In order to avoid this the crucible is supported in the neck of a flask with three constrictions, the neck extending above the top of the crucible and the latter being covered with a watch glass.

"Mineral Matter or Ash.—One gram of the same sample material used for the determination of bitumen is weighed out in a No. 0 Royal Berlin porcelain crucible and burned in a muffle or over a flame until free from carbon. This must be determined by breaking up the cake of ash, moistening with water or alcohol, and observing if any black particles of coke are present. The weight of the residue is stated as inorganic or mineral matter.

"The determination is, of course, not exact, sulphuric acid and the alkalis being volatilized in many cases, but it is satisfactory for technical purposes.

"Organic Matter Insoluble.—The amount of this material, sometimes stated as organic matter not bitumen, is obtained by difference, that is to say, by subtracting the sum of the percentages of bitumen and inorganic matter found, from 100. It, of course, includes all of the errors in these two determinations, and as the error in the bitumen determination is one making the percentage too high, and in that of the mineral matter too low, the errors are cumulative, do not neutralize each other and the percentage of organic matter not bitumen is thus always too high.

"If hot carbon bisulphide, chloroform or spirits of turpentine are used as the solvent for the bitumen the amount obtained on extraction is somewhat greater, but in technical work the results are no more desirable and such solvents are not often used, as chloroform is expensive when a large number of determinations are carried out and the spirits of turpentine is so much more viscous, that it filters much less readily, while the residue of it remaining on the filter must be removed by naphtha and not by evaporation.

"The sum of the three determinations, bitumen soluble in CS_2 , organic not soluble, and inorganic matter, is therefore, always 100 per cent.

"Naphtha Soluble Bitumen.—For the purpose of determining the percentage of bitumen soluble in naphtha distillates, 88° and 62° B. are used. It is extremely important that these naphthas should be of the exact degree specified, since differences in density will make an appreciable difference in the amount of bitumen extracted. The distillate should be

that obtained from a paraffine petroleum. The density of each lot should be determined with a Westphal balance at 60° F., and if it is too dense it should be rejected. On the other hand, if it is too light, it can be brought to the proper density by blowing a current of air through it for a short time, as the ordinary temperature in the case of the 88° and after slightly warming it in the 62° naphtha. Redistillation of these naphthas is unnecessary, as the products of distillation are no more uniform than the original naphtha.

"It will be found necessary that hard bitumens should be reduced to an impalpable powder before attempting to extract them, as otherwise the extraction will not be complete. The softer bitumens should be divided as much as possible.

"The bitumen is usually extracted with naphthas of both densities in order to determine the difference in their action. If the amount extracted by each is the same or nearly the same it will point to the fact that the bitumen consists of hard asphaltenes mixed with light malthenes, the latter equally soluble in naphtha of both degrees of density, and but little intermediate hydrocarbons, or of the very hard asphalts fluxed artificially with some light oil. If, on the other hand, there is a very considerable increase in the percentage dissolved by the 62° over the 88° naphtha it may be assumed that the malthenes are well graded and natural constituents of the bitumen which is being examined. In certain cases, however, the use of the two naphthas is unnecessary. It would be useless to extract maltha with a dense naphtha or a glance pitch or albertite with a lighter one. * * *

"All determinations are made with cold naphtha by the following method:

"One gram of the substance is weighed into a 200 c.c. Erlenmeyer flask, covered with naphtha and allowed to stand, as in estimating total bitumen, in fact, the entire process is the same with the exception that one or two precautions must be observed. It is well not to attempt to break up any lumps with a stirring rod, as the substance, especially the softer asphalts, may then adhere to the rod or flask and be difficult to detach. It may also be necessary to treat the substance with several portions of the solvent instead of two or three, as in

the case of carbon bisulphide. No heat is applied at any time in the process. * * *

"Determination of the Character of Malthenes or Naphtha Soluble Bitumens.—The determination of the relative proportion of saturated and unsaturated hydrocarbons which constitute the malthenes is very important in differentiating the soluble bitumens. It is made as follows:

"The 88° naphtha solution of the bitumen under examination is made up to a volume of 100 c.c. or reduced to that volume by evaporation. It is then placed in a 500 c.c. separatory funnel. An equal volume of the solvent naphtha is placed in another separatory funnel. The naphtha solution and the naphtha are then subjected to the action of 30 c.c. of sulphuric acid of specific gravity 1.84, the acid and naphtha being shaken together for exactly three minutes. This is most important, since the action of the acid on the hydrocarbons in the bitumen under examination is not a fixed one, but will continue more or less indefinitely. After the shaking, the acid and the naphtha solution are allowed to stand over night. The acid is then carefully drawn off and the shaking again repeated with another volume of acid of the same amount. This will require a shorter time for the separation of the acid and it can be drawn off within a few hours. If the second acid is very strongly discolored the acid treatment should be continued a third time. In the case of the blank treatment with the plain solvent one treatment will be sufficient. The naphtha solution and the naphtha are then washed twice with water and afterwards once with a 5 per cent carbonate of soda solution, after which one further washing with water takes place. The naphtha solution of the bitumen which is being treated and the blank naphtha are then poured into crystallizing basin $3\frac{1}{4}$ ins. in diameter and 2 ins. deep. In the plain naphtha is dissolved exactly 1 grm. of some extremely stable petroleum residuum. The two vessels are then placed upon the steam-bath to evaporate the naphtha. In order to avoid creeping the sides of the dishes are imbedded in a mass of cotton waste reaching to the top, as creeping is much diminished by having the sides of the dish warm. The evaporation is carried on on the steam-bath until the naphtha is

volatilized and until the blank shows on weighing that the residue has returned to its original weight of 1 gm. It is then assumed that the other dish is free from naphtha, and from the water which the latter has dissolved in the process of washing. This, under the conditions offered in the author's laboratory, will require about six hours, but the exposure on the water-bath is generally continued one hour after the blank has reached a constant weight and further for fifteen minutes on an air-bath at 100° C. as control. The results obtained in this way are of no absolute value, but are of relative value in comparing different fluxes and solid bitumens. It cannot, of course, be applied when the bitumen contains an appreciable amount of hydrocarbons volatile at 100° C.

"When 62° naphtha is the solvent its volatilization from the residue of bitumen which has been treated is extremely difficult, and such a determination is, therefore, not recommended.

"In some California residual pitches, which are derived from oils containing very considerable percentages of phenols, it may be preferable to treat the 88° naphtha solution with a solution of sodic hydrate of 25 per cent strength before the treatment with acid in order to remove the phenols. The phenols can be separated and identified by neutralizing the soda solution with acid.

Determination of Bitumen Soluble in Carbon Tetrachloride.—While in a large majority of cases the same, or nearly the same, amount of bitumen is dissolved by carbon tetrachloride as by bisulphide of carbon, bitumens are known in which hydrocarbons exist which are not as soluble in the former solvent—for example, one of the Venezuelan asphalts when overheated in refining, grahamite and some of the residual pitches. The use of the solvent may, therefore, be desirable at times for the purpose of differentiating the native bitumens. It is used cold in exactly the same way as carbon bisulphide. In the case of the grahamites, hot carbon tetrachloride dissolves an appreciable amount after the cold solvent has ceased to act. The residue on the Gooch crucible may, in this case, be removed to an Erlenmeyer flask and

treated further with the solvent. A definite result is more satisfactorily obtained with the cold solvent."

The numerous methods of analysis that have been described under this section are all modifications of one general process of separation of constituent principles that exist in solid bitumens, in relation to which chemists have assumed to know a great deal but really know very little. As a subject of chemical investigation a solid bitumen may properly be compared with a drug, which consists of a very complex mixture of organic compounds—like opium, for example. No pharmaceutical chemist would think of analyzing such a drug by subjecting it to distillation, which would almost certainly be destructive. The method employed would be one of percolation by solvents, resulting in a series of solutions which would be examined separately, yielding by elimination and exclusion, purified products that would in the end determine of what the mixture consisted in the beginning.

Boussingault's procedure was based on methods of proximate analysis that are not now applied to such problems. His somewhat fanciful names were based on wrong views concerning the composition of bitumens, that, by adoption into the nomenclature of recent years, under changed conditions, have only led to confusion. I think a perusal of the preceding pages fully demonstrates the truth of this statement.

The suggestion of Dr. S. P. Sadtler that solvents of fixed purity be employed in the analysis of solid bitumens is wholly sound. It is extremely unfortunate that a liquid so variable in composition and qualities as so-called petroleum ether or naphtha, should have been selected as a solvent for that portion of solid bitumens that is supposed to determine their quality for paving and other technical purposes.

This liquid is produced in different parts of the world, from such varied crude materials and under such varied conditions, as to be impossible of uniform qualities and chemical composition, even when possessing uniform physical properties such as are determined by specific gravity, boiling point, etc. I repeat that it is extremely unfortunate that a fluid of such uncertain properties should have been selected to answer the requirements of such a critical purpose.

If, however, those persons to whom the above considerations do not adequately appeal, continue to insist that petroleum ether shall be used in the analysis of solid bitumens, it should also be insisted that the volatile product of the petroleum refineries that is most constant in its composition and properties be carefully used, and not the heterogeneous distillates, the identity of which are supposed to be determined mainly through identity of specific gravity and other physical properties, that really determine little or nothing in regard to the composition and other chemical properties on which its chemical action depends.

My purpose, therefore, in writing the pages that follow is not alone to present a scheme, the use of which has been confirmed, by many years' experience to be, for all purposes, superior to any other, but, also to promote so far as my influence may promote, the use of solvents of fixed purity to the exclusion of any variety of naphtha or petroleum distillates of any kind.

The object of the technical analysis of solid bituminous minerals is not to determine the ultimate chemical composition of any of the complex compounds that may be mixed together to form the material under consideration, hence the method employed is more or less empirical.

The determination of the amount of whatever solubles may be selected gives results at the same time both absolute and relative. These results are of little value when taken singly and alone. They were suggested originally by an attempt to imitate the process described in Allen's "Commercial Organic Analysis," and it was for some time supposed by Miss Linton, myself, and probably by others, that a similarity existed in the materials dissolved by these same menstrua from different varieties of bitumen. I have some time since reached a conclusion that this is not the case.

In 1892 I distilled, under pressure, some California petroleum, and obtained a "cracked" distillate. I removed from this distillate the lighter portion and placed the residue remaining in the retort in a Becker glass, where a solid material gradually accumulated in a ring just below the surface of the liquid, and an addition of petroleum ether to the liquid pro-

duced a brown precipitate resembling ferric oxide when precipitated from its solutions. A precipitate having the same appearance can be thrown down from a turpentine, chloroform, or benzol solution of Trinidad pitch. I, for a long time, supposed they were the same substance—asphaltene—but they are entirely unlike. What relation, if any, they may bear to each other has not yet been determined. The precipitate from the California distillate appears to be wholly organic; that from the turpentine solution of Trinidad pitch appears to consist largely of a compound of alumina; while that from the chloroform soluble of the same bitumen appears to be an organic salt of iron. Technically these solutions, with their precipitates, bring into consideration certain problems concerning solid bituminous minerals of the highest importance. The result of an analysis that sets forth the specific gravity, melting point, flowing test, petroleum ether, and carbon disulphide solubles, with perhaps the total amount of nitrogen and sulphur, tells very little concerning the application to any particular purpose of any given specimen of bitumen. The term “organic matter not bitumen” is misleading, for in many cases the volatile matter so determined is not organic at all.

That which is of primary importance in the analysis of an asphaltic mineral is to learn what proportion of the mineral consists of hydrocarbons, soluble in solvents that will separate and distinguish them. If the volatile and combustible matter that appears as “organic matter not bitumen” is large in amount, it is of scarcely less importance to know exactly of what this material consists. Next in importance is the total amount and manner of combination of the sulphur; next the total amount and manner of combination of the nitrogen; and lastly, the total amount and manner of combination of the iron and alumina. The amounts of silica, lime, and magnesia should be known as guides in preparing the street mixtures, but they are of no significance in the determination of the specific qualities of the bitumen.

The method of analysis as described in Miss Linton's papers was the germ from which has been evolved by various modifications made by Miss Linton, my son, Dr. H. E. Peck-

ham, and myself, the following described apparatus and method of procedure, which has been tested in my laboratory by several years' constant and very successful use.

An ordinary retort stand is selected with a rod about 24 in. high. (Fig. 2.) A piece of brass tubing 10 in. in length,



Fig. 2.—Apparatus for Determination of Solid Bitumens.

with an external diameter of $1\frac{1}{4}$ in. and an internal diameter that will closely fit the rod, is soldered into a brass disk at either end 16 in. in diameter and $\frac{1}{8}$ in. thick. One of these disks is entire, the other contains 8 circular orifices equidistant from each other, the centers of which are $2\frac{3}{4}$ in. from the

circumference of the disk. The orifices are $2\frac{1}{2}$ in. in diameter, and are numbered I to VIII. The disks, with the orifices uppermost, are placed with the tube enclosing the rod so that they will rotate upon the rod at right angles with it.

Eight 200 c. cm. Erlenmeyer flasks are washed, dried, and weighed. They are then numbered 1 to 8, which with their respective weights are marked upon them with a diamond. These are placed beneath the corresponding numbered orifices in the upper disk. A second set of eight flasks is weighed, numbered and marked. In each of the orifices in the upper disk is placed a $2\frac{5}{8}$ in. Bunsen funnel, into the neck of which has been fused a glass stopcock of the best quality. The necks of the funnels below the stopcock should be ground at a bevel and should enter the flask about an inch. The funnels should be covered each with a 4 in. watch glass. With this apparatus four determinations can be made in duplicate at the same time.

The following groups of solvents may be used:

Either bisulphide of carbon, chloroform or benzole alone may be used to determine the total amount of bitumen, or

Petroleum ether, and bisulphide of carbon;

Petroleum ether, and chloroform;

Petroleum ether, boiling spirits of turpentine and either bisulphide of carbon or chloroform.

Distilled water followed by 95 per cent methyl alcohol, ethyl ether and chloroform.

Distilled water followed by acetone, ethyl ether and chloroform. Each of these combinations of solvents if used on a series of bitumens tells its own story and furnishes its own data by which to distinguish the members of any series from each other. I have used all of them and each is to be recommended for special purposes and occasions.

Bisulphide of carbon is cheap, expeditious, disagreeable and very inflammable.

Chloroform is expensive, agreeable and non-inflammable. Moreover, it is a more certain and complete universal solvent for all classes of bitumens than any other liquid.

Boiling spirits of turpentine determines the group relations of many bitumens with great exactness and has been

found by the author, ever since Miss Linton first proposed its use, to give frequent and valuable testimony in the analysis of bitumens, but, the objections urged against its use by Dr. Sadtler and others are admitted to be sound. Nevertheless, the group petroleum ether, followed by boiling spirits of turpentine, followed after washing by chloroform, is a group that experience is likely to retain for occasional use.

I have elsewhere* shown that acetone does not furnish results that are comparable with those furnished by petroleum ether. I am, however, convinced that the scientific investigation of bitumens would make much more rapid progress if Dr. Sadtler's suggestion that solvents of fixed purity should be universally adopted in all researches on solid bitumens even at a cost of time and money and the establishment of a new series of constants. For, chemists have got to build on a more solid foundation than assumptions and probabilities, and the generalities expressed in the general classifications of saturated and unsaturated compounds before any strictly scientific knowledge will be gained concerning the composition of bitumens.

Acetone is more nearly allied to the alcohols than to the pure hydrocarbons, and therefore dissolves substances that are wholly insoluble in hydrocarbons. In illustration, two samples of Trinidad pitch. No. 1, a sample of crude pitch. No. 2 a sample of *Epurée*, made on the island, were analyzed by the use of petroleum ether and acetone with the following results:

No. 1.	
Petroleum ether soluble.....	33.736
Boiling spirits turpentine soluble...	10.511
Chloroform soluble	8.120
Organic matter not bitumen.....	10.851
Inorganic matter	36.729
<hr/>	
99.937 per cent.	
No. 1.	
Acetone soluble	28.180
Chloroform soluble	27.005
Organic matter not bitumen.....	9.835
Inorganic matter	34.980
<hr/>	
100.000 per cent.	

*Jour. Franklin Institute, March, 1896.

No. 2.		
Petroleum ether soluble	33.625	} 51.875 total bitumen.
Boiling spirits turpentine soluble....	15.575	
Chloroform soluble	2.675	
Organic matter not bitumen.....	10.150	} 48.125 non-bituminous ma-
Inorganic matter	37.975	
		100.000 per cent.

No. 2.		
Acetone soluble	26.310	} 55.48 total bitumen.
Chloroform soluble	29.170	
Organic matter not bitumen.....	9.600	} 44.52 non-bituminous mat-
Inorganic matter	34.920	
		100.000 per cent.

	No. 1.		No. 2.	
	Petroleum Ether.	Ace- tone.	Petroleum Ether.	Ace- tone.
Total bitumen	52.367	55.185	51.875	55.480
Non-bitumen	47.580	44.815	48.125	44.520

To still further test the relation of the two solvents, equal portions of a very dry Egyptian asphaltum were exhausted under identical conditions with petroleum ether and acetone. The results are given below:

	Per cent.
Petroleum ether soluble.....	38.03
Acetone soluble	8.68

Also, an Athabasca River maltha was exhausted in the same manner, with the following results:

	Per cent.
Petroleum ether soluble.....	73.863
Acetone soluble	24.333

No difference was observed between the solvent power of cold and boiling acetone in either case. The dry Egyptian asphalt and the semi-fluid maltha exhibit the extremes to which any solvent of bitumen is likely to be applied, and the lack of parallelism is enormously large in both cases.

After several years' experience I am satisfied that the simplest as well as most satisfactory method of procedure is as follows: The solvents should be freed from water. The petroleum ether and chloroform should be agitated with strong sulphuric acid and distilled over caustic lime, or dry

sodium carbonate, with steam. The turpentine should be shaken with freshly burned lime, poured off, and rapidly distilled. A rapid method which removes the water but does not otherwise purify these liquids, consists in thorough agitation with dry powdered plaster of Paris. Apparently all of these liquids are sold with all of the water they will hold.

The filters that I use are those prepared by Baker and Adamson, 11 cm. in diameter, which have been washed with both hydrochloric and hydrofluoric acids. These filters are not appreciably affected by the solvents. Three of them are balanced, and two are placed in separatory funnels, into which are weighed such portions of the bituminous mineral as will assure about half a gram of bitumen. The filter is filled with petroleum ether, which is allowed to run through slowly until the color has perceptibly diminished, and then the stopcock is closed between each addition of solvent for 15 to 30 minutes, until the solvent passes colorless. It is well to leave the funnels to stand over night at the end, but not at the beginning of the operation. All three filters are dried in the air, then in an oven, at about 150° F., and weighed. Very close work can be done in this way. The solution may be tested with fuming nitric acid, or may be evaporated, and the residue treated with nitro-sulphuric acid, or 10 per cent sulphuric acid for basic oils. The dried filters are returned to the funnels and exhausted as rapidly as possible with boiling spirits of turpentine. The turpentine should not be allowed to cool in the filters. When the exhaustion is complete the filters are washed with petroleum ether by filling the closed funnel above the filter to complete submergence and allowing the filter to digest for 30 minutes. A second digestion will usually completely remove the turpentine. The filters are then dried and weighed. The turpentine solution may be diluted with several times its volume of petroleum ether and the precipitate examined by treatment with nitric acid, etc.

The dried filters are again returned to the funnels and after being exhausted with chloroform are again dried and weighed. The chloroform may be distilled off and the residue washed in petroleum ether and tested.

The dried filters are again returned to the funnels wetted with alcohol, and after exhaustion with 10 per cent hydrochloric acid, are washed, dried, and weighed. The loss is calcium and magnesium carbonate and calcium sulphate, if any is present. The calcium, magnesium, and sulphuric acid may be determined in the acid solution if desired, also iron and alumina, if any are present.

The filters are cut in small pieces and deflagrated with sodium carbonate and potassium nitrate, and sulphur, as pyrites, silica, iron and alumina, are determined in the fused mass.

A new portion of the bituminous mineral, containing at least $\frac{1}{2}$ gm. of bitumen is deflagrated with sodium carbonate and potassium nitrate, and in the solution of the fused mass silica, sulphur, iron, and alumina may be determined, or lime and magnesia, if they are present.

Nitrogen may be determined by any method desired. A portion is dissolved in pure chloroform and the solution washed with 10 per cent dilute sulphuric acid. The acid solution is neutralized with sodium hydrate, when nitrogenous basic oils will be recognized by their odor. Another portion is exhausted with chloroform and the residue extracted with ammonium hydrate for the peat, or other organic acids.

Free sulphur will be found in the petroleum ether solution. Organic compounds of alumina will be chiefly found in the turpentine solution. Very few natural, solid bitumens are free from at least a trace of these curious and little-known substances.

"Organic matter not bitumen" consists of coke, peat acids and humus, partially decayed woody fiber and sulphur. If the bitumen contains ferrous sulphate or pyrite, the sulphuric acid or sulphur will be lost here and the iron will appear in the residue saturating the filter ash as colchotha, as is not infrequently observed.*

Another method of procedure that requires more time, but which gives more satisfactory results is as follows:

From 0.5 gms. to 5.0 gms. of the samples are weighed in duplicate into the second numbered series of Erlenmeyer

*Jour. Soc. Chem. Ind., xvi, May, 1897; xvii, May, 1898.

flasks, the numbers corresponding to the numbered funnels and receiving flasks. Fifty c. c. of petroleum ether or acetone is poured into the flasks which are closed with a good cork and set aside with occasional shaking, preferably over night. The sample should not be pulverized, as pulverizing would destroy, in the residue, materials that distinguish some of the bitumens. The use of a Gooch crucible has the same result, destroying organic forms and changing mineral constituents of residues, that are characteristic of some of the bitumens.

When the fragments of bitumens are broken down the contents of the flask are decanted upon the filter in the corresponding numbered funnel. Other portions of the solvent are added to the flask in small portions, successively, and after agitation and subsidence, are decanted upon the filter. This is repeated until the filtrate passes colorless. The flask containing the filtrate is allowed to rest from 12 to 48 hours, when the liquid is carefully decanted into another flask and preserved for further examination. The flasks and filters are air dried, then dried at 220° F. and weighed, after cooling, in the air of the laboratory.

Experiments made during many years have proved that the fine residue that settles from the above filtrate is as varied in composition as the bituminous materials under examination. It is seldom or never wholly a mineral residue, but usually, especially in the case of crude natural bitumens, it consists of organic salts that can be dissolved in suitable solvents forming transparent solutions, from which they can be precipitated as amorphous solids. Such reactions are not characteristic of a suspended solid, no matter how finely divided it may be nor how long it may take to subside.

The weighed filters are returned to their respective funnels. Pure doubly refined spirits of turpentine is poured upon the residue in the flask last decanted, and boiled. While boiling the flask is rinsed and the hot solution is poured into the flask containing the bulk of the residue. The turpentine is again brought to a boil, allowed to subside a moment and poured through its numbered filter into the first flask. In this way the residue in both flasks and the funnel is brought under the action of the boiling turpentine, which will com-

pletely dissolve many natural bitumens and most residuums. The two flasks and the filter are washed with petroleum ether until the turpentine is completely removed, when they are again dried and weighed.

The residues in the flasks are treated with pure chloroform and the solvent passed through the filter. The filter and flasks are dried and weighed.

The sum of the amounts dissolved in the different sets of solvents represents the total amount of bitumen present.

In residual pitches the residue remaining may consist of nothing but coke. In natural bitumens it consists of much or little of a variety of substances. The filter may be moistened with alcohol which may be allowed to percolate into one of the flasks and after moistening the interior thereof, the liquid may be poured into the other flask. If this precaution is not taken, the next solvent used, consisting of dilute hydrochloric acid (1—9) will be repelled from the surfaces without wetting them. This dilute hydrochloric acid will decompose all of the carbonates present, but it will leave the silica, clay and pyrite untouched. The organic matter not bitumen will also be undissolved. The residue remaining should be thoroughly washed with distilled water and carefully air dried. The dried material should then be carefully examined under a microscope of low and high power. There will be recognized:

The wing cases of insects.

Fragments of vegetation, including partially decayed wood.

Clay.

Fragments of crystals of quartz.

Grains of quartz of various forms.

Pyrite, in grains or crystals, some of them very minute.

Other organic or mineral forms rarely occur.

I fully agree with Mr. Dow in his judgment respecting the use of different forms of the Soxhlet apparatus. This apparatus in several forms, suggested by experience, was given a very thorough and prolonged trial in our laboratory and given up as impracticable not only for the reasons given by Mr. Dow, but also for the form of the filter, the unavoidable spattering of the contents and the generally difficult manipulation which it inevitably required.

I have gone back to my filters and separating funnels and normal temperature of the laboratory, from every attempt to use the Soxhlet apparatus, the Gooch crucible or Mr. Dow's test tubes. No apparatus or method of analysis by percolation fulfils all of the requirements suggested by theoretical considerations, nor is any apparatus or method free from criticism. The selection depends upon a maximum of information respecting the specimen under examination obtained for the least expenditure of time, reagents, risk of fire and other accidents, with a minimum of sources of error. Without denying any of the claims made for other methods, I have found the method contrived by Miss Linton to fulfill the above named requirements best.

Concerning solvents, I have used all that have been suggested. I think before any really scientific knowledge is gained concerning the chemistry of bitumens, chemists will have to abandon the wholly empirical methods of analysis based upon the use of petroleum distillates and carbon bisulphide and take up in earnest the tedious, but fruitful, methods requiring the use of solvents of fixed purity, suggested by Dr. S. P. Sadtler. These liquids are alcohols, of not less than 95 per cent purity, acetone, commercially pure, ethyl ether and chloroform. Carbon tetrachloride may perhaps be added to this list. I am confident that with these solvents natural bitumens will eventually be separated by constant reactions from residual pitches and both classes of substances will be separated into their constituent compounds of fixed composition, which through their substitution compounds will be referred to their proper places and relations with systematic names, not fanciful names, based upon assumptions and probabilities, often misleading, and never final.

I have made use, with increasing frequency, of commercially pure acetone, in all varieties of investigations of bituminous materials. Its composition is practically constant. Its reactions are equally so. Its reaction upon coal tar pitches are very characteristic. It is of the highest efficiency in the separation of natural bitumens. In the investigation of wood paving blocks, saturated with mixtures of which genuine creosote oil forms a part, it is unequaled. While it is very volatile, it is not so extremely volatile as the petroleum

distillates of high specific gravity, which it is designed to displace. Boiling at 80° C. it is easily expelled from the residues it dissolves. Followed by ether and chloroform or ether alone, the three solvents appear to really analyze bitumens and not to separate them into empirical mixtures as complex as the original substance. Moreover, it is innocuous to the operator.

With this admittedly inconclusive discussion I leave a subject that is becoming, I believe, one of the most fruitful fields of chemical research, presented to the chemists of this opening century.

CHAPTER XIII.
SPECIAL CHEMICAL AND PHYSICAL METHODS OF
ANALYSIS BY WHICH SOLID BITUMENS MAY
BE RECOGNIZED AND DISTINGUISHED.

FIXED CARBON.

The estimation of fixed carbon by the following described method, is found to furnish data that are of value in the determination of the different varieties of solid natural bitumens, and their separation from each other and from residual pitches and other forms of "Factice." The method of determination is as follows:

Place one gram of the bitumen in a platinum crucible holding 30 c. c. and with a tightly fitting cover. Heat over the flame of a Bunsen burner for five minutes. Some operators recommend seven minutes, but I have found five minutes to be ample. The volatile matter burns off in from one to two minutes. The crucible should be supported on a platinum triangle so far above the top of the burner as to bring the bottom of the crucible 6 cm. above it. The flame should burn free about 20 cm. high, and the crucible should be thrust into it in such manner as to immediately receive the full effects of it. The upper surface of the cover and the sides of the crucible will immediately burn clear, but the under surface of the cover and the inside of the crucible will remain covered with a thin film of carbon. The flame should burn free from draughts.

The crucible and cover are weighed and the loss computed as "volatile matter."

The carbon is then burned off the cover and the crucible is again placed in the flame and the combustible matter fully burned off, leaving nothing in the crucible but the clean ash. After weighing, the second loss is computed as "fixed carbon."

Both these constants are very certain in a given specimen, and may be duplicated with great accuracy. They are

wholly empirical data closely resembling the volatile and fixed carbon of coal but with the ash they furnish a valuable means of identification and separation.

The natural bitumens are usually high in ash and fixed carbon. The specimens of "Factice" are nearly or quite free from ash and low in fixed carbon.

The bituminous rocks form a class by themselves. The bituminous lime and magnesian rocks cannot be burned for fixed carbon, as the carbonic acid present in the rock is added wholly or in part to the volatile combustible matter. In the case of rocks containing carbonates, the bitumens should be dissolved from the mineral matter in chloroform, the solution evaporated at a low temperature and the bitumen then treated as if it were an original specimen.

STREET MIXTURES AND SURFACES.

Street mixtures should never be pulverized. They should be rubbed in an iron mortar only sufficiently to prepare an average sample. Street mixtures of good quality are pulverized with great difficulty. The poorer ones may be easily reduced to a powder but little if any finer than the sand used. If the sand is reduced to a fine powder many characteristics that serve to identify the bitumen will be destroyed. Five grams of the prepared sample are weighed into duplicate, balanced filters and exhausted with chloroform or bisulphide of carbon. If any of the finely divided mineral aggregate passes the filter, the filtrate should be allowed to stand at rest at least twelve hours, or over night, when the liquid is decanted from the matter that has subsided, the subsided matter washed with a fresh portion of the solvent, the flask dried, wiped clean and weighed. The weight marked on the flask is subtracted from the total weight and the difference added to that of the residue remaining in the filter. The sum of the weight of the residues remaining in the two filters subtracted from 10 gms. gives the mean percentage of the bitumen found in the two duplicate samples.

The residues when moistened with alcohol, treated with dilute (1—9) hydrochloric acid, washed with distilled water dried and weighed, show a loss which represents the percentage of carbonates in the asphaltic mixture. Besides the carbon-

ates, there may be a small and varying percentage of matter dissolved from pulverized trap-rock or other rocks which form a part of the mineral aggregate used. For technical purposes, this error, while it is recognized, may be disregarded.

The washed and dried residue should be carefully examined under a microscope, and then burned, if such treatment is desired.

Surfaces that have been laid should be carefully separated from any binder that may adhere to the specimen, or any pieces of rock or gravel that may have been pressed into them. The surface should then be treated precisely as if it were a mixture.

Surfaces that have been laid for some months or years will be found to vary in total bitumen from the surface downward.

It will be often found advisable to use the three-solvent method in the examination of mixtures and surfaces.

Great differences will be observed in the action of solvents upon mixtures and surfaces containing different kinds of bitumens. Trinidad pitch and mixtures containing it, forms, with all solvents, a more or less viscous solution that filters slowly, leaving the filter stained with peculiar black markings that are readily distinguished when once observed. Other bitumens filter more readily, leaving the filters discolored in their own peculiar manner, that may be readily recognized. Residual pitches from coal tar are not readily soluble in petroleum ether, but dissolve in acetone, forming an opalescent solution of a pale amber color. These pitches usually leave a filter discolored with finely divided coke. Residual pitches from petroleum are acted on by solvents very readily and leave a filter nearly as clean as at the beginning. Experience soon teaches the operator with Miss Linton's filters to recognize a large number of data difficult to describe but furnishing very constant characteristics from which the kind of bitumen may be distinguished.

FUMING SULPHURIC ACID TEST.

(Malo—Durand-Clayè—Meinecke.)

According to Leon Malo, the following, originally proposed by Durand-Clayè, serves in the laboratory of the "Ecole

des Ponts et Chaussées," in Paris, to distinguish the difference between natural and artificial asphalts. The substance under examination (most likely a specimen of either stamped or molded asphalt) will after separation of the mineral constituents by extraction with carbon bisulphide and the evaporation of the solution to a residue, be dried by careful warming until it becomes firm and brittle. It is then pulverized. In a test tube upon 0.1 gm. is poured 5 c. cm. of fuming sulphuric acid at 66° B. The specimen is left to stand for 24 hours and is then slowly diluted, from a pipette with 10 c. c. of water, avoiding an excess of heat. It is then brought upon a filter and washed with sufficient water to make 100 c. cm. The filtrate from pure natural bitumen is colorless or at most slightly colored; that from coal tar pitch is dark brown inclining to black.

C. Meinecke shakes 0.1 gm. of the ash-free asphalt with 10 c. cm. of fuming sulphuric acid (strong) which reveals remarkable differences, especially in a thin stratum, also by lowering and raising the test tube, that it may flow back slowly on the interior surface. As the liquid flows back, it is, in the case of:

- (1) American asphalt, brown running into gray.
- (2) Syrian asphalt, brown.
- (3) Trinidad asphalt, brown.
- (4) Brown-coal tar pitch, gray inclining to brown.
- (5) Coal tar pitch, gray black, trace of greenish, streaky (from particles of coal).

From this it may appear that the natural asphalts give brown, and the artificial, gray mixtures.

Meinecke remarks further, that in these mixtures of sulphuric acid after standing 24 hours and being tested by the microscope, more or less coking can be observed in the different asphalts. Coal tar pitch is sharply different from the asphalts through the intensive blackness due to the proportionately large particles of carbon, of nearly the same dimensions, that are arranged in planes. The asphalts of Syria, Trinidad and America, as well as brown-coal tar pitch, show similar particles, so that a difference in this way is scarcely possible to determine.

The reaction of Durand-Clayè in the manner set forth in the above mentioned sulphuric acid mixture poured with shaking into between 15 and 20 c. c. of water and filled up to 100 c. c. gives, when filtered and poured into a test tube 18mm. wide, according to Meinecke, the following results:

- (1) American asphalt, pale yellow-brown solution.
- (2) Syrian asphalt, yellow-brown, clearer than No. 1.
- (3) Trinidad asphalt, yellow-brown, clearer than sherry.
- (4) Brown-coal tar pitch, dark brown; it does not permit itself to be read through.
- (5) Coal-tar pitch, black, opaque.

To prove the presence of coal tar asphalt in natural asphalt, Leon Malo uses the Durand-Clayè reaction to approach by a colormetric way a determination of the sophistication of the mass, as samples of natural asphalt mingled with different percentages of coal-tar pitch impart for each percentage a certain intensity of color to the aqueous filtrate.*

ALCOHOL AND ALCOHOL-BENZINE TESTS.

Hauenschild.

The proof of coal-tar pitch in natural asphalt succeeds, according to Hauenschild, most easily, when 1 gm. of the material is heated to 200°, then, after cooling, pulverized and immersed in about 5 c. c. absolute alcohol. After standing in a test tube a short time, the content of coal-tar pitch is shown through the yellowish color of the alcohol with a slightly green-blue fluorescence, in which with an increasing proportion of pitch, the dark yellow is changed into the yellow-green fluorescence.

A more general method even than that of Durand-Clayè is found in the different behavior of natural and artificial bitumens with benzine and alcohol. Upon 1 gm. of the pulverized product is poured 5 gms. of rectified benzine in a closed glass vessel and shaken until the solution appears deep black. The solution is filtered and five or six drops of the filtrate are dropped into a test tube containing 5 c. c. benzine and an equal amount of strong ethyl alcohol. After vigorous shaking the solution is left at rest, when there will appear an upper benzine layer separated from a lower alcohol layer.

*Ann. des Ponts et Chaussées, 1879, vol. 2.

It is then subjected to successive benzine-alcohol treatments. The coloring of the third solution discloses whether the natural asphalt has been falsified with coal-tar pitch. If it is colorless or only slightly yellow, then the asphalt is pure; if it shows a golden brown coloring, then it contains coal-tar pitch.

Mixtures of bitumen and pitch show mezzotints; in this colormetric way, a proportion of from 10 to 20 per cent of coal-tar pitch can be proved to be present.*

PRECIPITATION METHOD.

Kovács and Sötét.

According to J. Kovács it is impossible to determine quantitatively the falsification of an asphalt by petroleum residuum in less proportion than 20 to 25 per cent, but the presence of an additional quantity can be proved by the following, communicated and worked out in association with S. Sötét.

A sample of the asphalt to be examined is treated with carbon disulphide and the filtered extract evaporated to a dry residue at 110° C. The dried residue is dissolved in two and one-half times its weight of carbon disulphide, and at the same time an equal concentrated solution of pure asphalt in carbon disulphide is placed beside it.

One c. c. of the solution is poured into 2½ c. c. of oil of turpentine in a test tube. If the product contains coal-tar pitch, a light brown solution and a light brown precipitate is obtained, while the solution of natural asphalt remains dark colored and gives no precipitate.

The original solution is treated with absolute alcohol in the proportion of 1—10, when the coal-tar pitch appears as a brown precipitate; natural asphalt furnishing a black, sticky pitchlike precipitate, while petroleum pitch furnishes a fine, black, flocculent precipitate. If the precipitate is filtered off and dried at 90° to 95° C. that from coal-tar pitch is like flour, is dull and of a light brown color, while that from natural asphalt is black, sticky, brilliant and when warmed can be drawn out into fine threads. Under the same conditions, pe-

*See E. Dietrich, *Die Asphaltstrassen*, p. 44; Durand-Clayé, *Nöthling, Der Asphalt*, p. 35.

roleum residuum gives a precipitate black, dull, earthy and easily broken between the fingers.

One c. c. of the original solution, shaken with 5 c. c. of absolute alcohol, furnishes with coal-tar pitch a brown precipitate and a black pitch like scum, petroleum pitch a black, muddy precipitate, whilst pure asphalt gives a black precipitate or pitchlike coherent scum. The supernatant fluid above the precipitates is reddish brown with petroleum pitch, and light brown with coal-tar pitch and pure asphalt.

The filter paper spread out and dried at 90° to 95° C., shows precipitated upon it, with coal-tar pitch and asphalt, glistening, pitchlike material, sticky and adhesive after warming; while petroleum pitch on the contrary, yields a muddy, friable mass leaving behind transparent, oily, red-brown spots upon the paper.*

The cohesive properties of the bitumens obtained from natural asphalts and solid bitumens explain the superior qualities exhibited by these materials when used for paving and other purposes, when compared with the various forms of factice produced by artificial methods.

DETERMINATION OF PARAFFINE.

Krämer and Spilker.

Of the component constituents of natural asphalt, there is only a single one —paraffine—that has been separated in a condition of purity. For the determination of the same, I describe a method which Kramer and Spilker have given for the determination of paraffine in raw anthracene as follows:

Ten gms. of the bitumen, very finely pulverized, are mixed in a 100 c. c. graduated cylinder with 70 c. c. of ether, agitated for some time, filled up to the mark with ether and set aside. Fifty c. c. of the clear solution is brought by means of a pipette into a porcelain dish, left until the ether evaporates and the residue dried for half an hour at about 100° C. The cooled residue is then made as fine as possible in the dish and 8 c. c. fuming sulphuric acid, added, the whole being well mixed and heated, in the dish for two hours with frequent stirring at about 100° C. The contents of the dish are

*Chem. Rev. d. Fett u. Harz-Ind., 1900, p. 8; 1902, p. 156; Jour. Soc. Chem. Ind., 1901, p. 564; 1902, p. 1077.

washed into a Becker glass with 500 c. c. of hot water, cooled, and filtered through a damp filter. The Becker glass and filter are washed with cold water until barium chloride indicates no cloudiness.

The filter is allowed to drain well, is thoroughly wetted with absolute alcohol, and the paraffine washed out by pouring ether through the filter into a tared dish until a drop of the escaping ether when evaporated leaves no residue. Also the last particle of paraffine is removed from the Becker glass by means of ether.

The ethereal solution will soon evaporate in a warm place, the residue dried therein for a half hour and the paraffine weighed.*

Richardson and Holde.

Clifford Richardson has applied the method proposed by Holde for the determination of paraffine in oils, to a research upon "The Determination of Paraffine in Petroleum Residues, and Asphaltic Oils and Asphalts Fluxed with Paraffine Oils." For this purpose 1, 2 or more gms. of the substance to be examined are taken and treated in an Erlenmeyer flask with 100 c. c. of 88° petroleum naphtha. The naphtha is allowed to act on the substance over night and the next morning the solution is decanted through a Gooch crucible, the residue washed with naphtha and the solution and washings united, and shaken in a capacious separatory funnel with sulphuric acid of sp. gr. 1.84 until a new portion of the acid is no longer colored. As a rule two washings are sufficient. The paraffine solution is washed with water, then with a weak solution of sodium carbonate and again with water; in this manner the mixture of paraffine and asphalt hydrocarbons, freed of all unsaturated hydrocarbons, is isolated by evaporation of the solvent.

According to the method of Holde, the residue is taken up with ether and the asphalt hydrocarbons are precipitated therefrom by addition of alcohol. The paraffine is obtained in a pure state by evaporation of the filtrate.

Determinations by this method gave the following results:

*Muspratt *Chemie*, 4 ed., vol. 8, p. 70.

PETROLEUM RESIDUUM FROM PIPE LINE OIL.

Sp. Gr. 0.93.

	Weight G.	Per cent of Soluble in Naphtha.	Per cent Not Acted on by H_2SO_4 .	Per cent of Paraffine.
No. 1.....	11	96	No treatment	7.95
No. 2.....	11	96	89.5	5.55
No. 2.....	11	Distilled in vacuo	No treatment	5.95

TRINIDAD ASPHALT CEMENT.

	Weight G.	Per cent of Soluble in Naphtha.	Per cent Not Acted on by H_2SO_4 .	Per cent of Paraffine.
No. 1.....	10.0	Not washed	2.95
No. 2.....	10.0	Not washed	0.95

In every case the recovered paraffine, after treatment with acid, was white, and pure, whilst by means of vacuum distillation it could only be obtained colored. The results were something lower, but more correct than those obtained by vacuum distillation.

The Trinidad asphaltic cement was made from 100 parts Trinidad asphalt and 20 parts petroleum residuum containing 5.55 per cent of paraffine. The Trinidad asphalt was paraffine free, the calculated amount in the cement was 0.925 per cent whilst 0.95 per cent was found.*

ARTIFICIAL ASPHALTS.

The artificial asphalts, as a rule, contain free carbon, in an amorphous condition as an insoluble constituent; proceeding from decomposition incident to the destructive distillation of organic substances, with which a greater or less quantity of ash constituents are rarely associated.

The determination of the soluble bitumens of artificial asphalts can be made in a similar manner as with the natural asphalts, with this difference, that, as a rule, the content of free carbon is ascertained and the quantity of bitumen calculated out of the difference. With the artificial asphalts which have been obtained through distillation of mineral coal from common coal-tar through all stages to coal-tar pitch, the ascertaining of the proportion of soluble bitumen is generally practicable only by a calculation of differ-

*Journal Soc. Chem. Ind., 1897, p. 16; 1902, p. 690. Mittell aus der Königl. Versuchsanstalt zu Berlin, 1896, p. 211.

ence, because by the evaporation of extracts, and particularly by drying the residues from the distillation, such volatile substances as the low boiling hydrocarbons, and also those with high boiling points like naphthalene are lost.

As a rule the object is obtained when the product is boiled out with twenty times the quantity of benzole hydrocarbon (xylol) and brought upon a filter with water white hot hydrocarbon and washed out until the filtrate flows uncolored.

Köhler (Ding. Poly. Journal 270, p. 233) has found a mixture of equal parts of Toluole and glacial acetic acid to answer the purpose. Kraemer and Spilker (Muspratt Chemie 4 Edition, Vol. 8, p. 3) as a most convenient practical method offer the following:

Warm one part of tar or of the pulverized artificial asphalt with 3 parts anilin and pour the semi-fluid mass upon a small plate of burned unglazed porcelain. The solvent together with the soluble constituents of the tar or pitch will be absorbed by the porous mass, while the insoluble carbon remains behind as a laminated mass, that, with a small wooden spatula can be brought without loss upon a tared watch glass, that after more than an hour in the water bath will be brought to weight. According to the above named authors, the extraction of bitumen by means of anilin is more complete than by means of the previously mentioned hydrocarbons.

DISTINGUISHING BETWEEN ARTIFICIAL ASPHALTS.

Davies.

The difference between the artificial asphalts out of coal-tar pitch, brown-coal-tar pitch, wood-tar pitch and candle-tar pitch, is determined by slightly heating the bitumen over an open flame. The escaping odor is characteristic of each pitch and quickly reminds one in the tar pitches of the specific smoke of the respective tar, and for candle-tar pitch, of burning fat. Their behavior with petroleum benzine is also useful, in which coal-tar pitch is the most difficultly soluble and in the smallest quantity, whilst brown-coal-tar pitch is

nearly wholly soluble therein. The behavior of the wood-tar and candle-tar pitches, in these solvents is, according to Davies, as shown in table:*

	In Petroleum Benzine.		Ash.	Sulphur.
	Soluble. Per cent.	Insoluble. Per cent.	Per cent.	Per cent.
Wood-tar Pitch, 1.....	24.44	75.56	0.20	0.69
Wood-tar Pitch, 2.....	18.70	81.80	1.06	0.41
Wood-tar Pitch, 3.....	15.86	84.14	0.48	0.59
Candle-tar Pitch	71.05	28.95	5.50	0.04

According to Buchanan even the origin of the different kinds of coal-tar pitch (coke-oven or gas or blast furnace tar), can be determined with certainty through the percentage of ashes. Tar pitch never contains more than 0.1 per cent, the latter 6.8 per cent to 11.1 per cent of ash; if then, a coal-tar pitch contains less than 1 per cent of ash, it is certainly no coke-oven pitch. As the asphalt industry involves the cohesive strength and elasticity of all these kinds of pitch this remark is not without interest.†

Separation of the natural and artificial asphalts and proof of the latter in mixture with the former.

In order to ascertain the difference between coal-tar pitch and natural asphalt (the mixture seldom contains brown-coal-tar or wood-tar pitch), in most cases it is sufficient to heat the sample in a crucible, at the same time distinguishing the heavy stinging odor of the coal-tar pitch from the bituminous odor of the natural asphalt. Very characteristic also is the conspicuous green-blue fluorescence which appears in a weak solution of the tar-pitches in benzol, carbon bisulphide, chloroform, benzine, and especially acetone.‡

MICROSCOPE.

Meinecke.

As E. Meinecke has shown, the microscope also reveals the nature of the molecular condition of the asphalt. He spreads the microscopic preparation upon a heated slide. Syrian asphalt exhibits when viewed under the microscope,

*Chemist and Druggist, xxv. p. 504. Scheithauer, Muspratt's Chemie, 4 ed., vol. 6, p. 1982.

†Jour. Soc. Chem. Ind., 1894, p. 1098.

‡Lunge-Köhler, Ind. des Stein Kohlen Teers u. Ammonlaks, 4 ed. 1, p. 436. 436.

a yellow-brown, transparent, homogeneous mass. Quite similar, yet not so intensely colored, appears the brown-coal-tar pitch under the microscope, while coal-tar pitch contains innumerable particles of carbon, that stand out against the golden yellow ground. In Trinidad asphalt is found a yellow-brown ground with larger and smaller little kernels of mineral matter, between which are small particles of an unknown nature (coal?). Viewed through crossed Nicol's prisms, the prepared slide gives nothing of striking value.*

SPECTROSCOPE.

Kayser.

According to R. Kayser the spectroscopic department of the different asphalts is a satisfactory means by which to distinguish the natural from the artificial products. Concerning the nature of this research, he refers to H. W. Vogel's "Praktische Spektral-analyse irdischer Stoffe." For research upon the absorption spectra, Kayser recommends a solution of the asphalt in chloroform of a slight intensity of color. Figs. 3 to 14 exhibit a graphic representation of the results obtained by those experiments. Especially characteristic of Syrian and Trinidad asphalts are the lines between D and E, with α , β and γ , indicating absorption bands, by which upon thin solution in spirits of wine and ether these constituents are separated as the same bands are not shown in the insoluble portion. The portion soluble in alcohol is differentiated from that soluble in ether by the strong absorption band γ , which does not appear in the ether solution, although the latter exhibits the β band much stronger.

The absorption spectra of the asphalt of Pechelbronn and its constituents, as well as the asphalts out of coal-tar do not show this band.†

The preceding pages (196 to 207) present a series of empirical tests that taken separately are of little value, but when used successively in a series, and especially when undertaken by an experienced manipulator, furnish conclusive evidence as to the kind of pure or mixed bitumen under examination.

*Chem.-techn. Unters. über Trinidad-goudron, Bleibrich, Verlag von Mattar u. Gaszimus.

†10c, cit. p. 29; D. H. Köhler Chem. u. Tech. der natürlichen u. Künstlichen Asphalte, Brannschweig, 1904, p. 346.

Quantitative results are only approximately satisfactory, yet they are not without value.

I make the following comments on the different tests mentioned.

In general it may be stated that brown-coal-tar pitches are almost unknown in the markets of the United States. Straight coal-tar pitches are less rarely used than those pro-

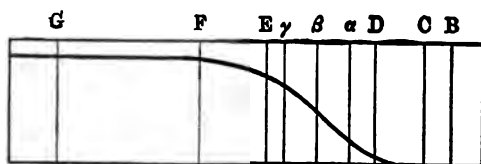


Fig. 3.—Asphalt of Bechelbronn.

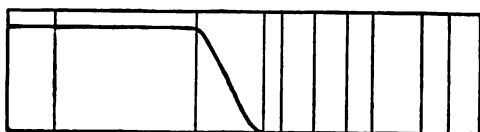


Fig. 4.—Petrolene from 3.

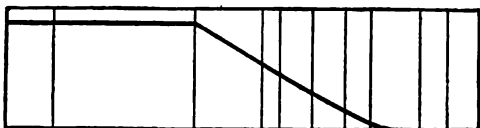


Fig. 5.—Asphaltene from 3.

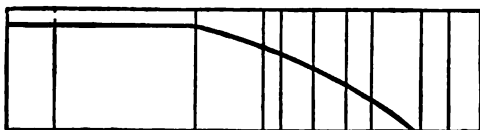


Fig. 6.—Coal Tar Asphalt.

ceeding from a modified process for producing gas in which the distillation of coal is supplemented in various ways. To these are added coke-oven-tar pitches and blast-furnace-tar pitches, thus furnishing a variety of pitches that give modified and slightly varying results that have a general likeness to each other and difference from true asphalts and petroleum pitches.

While specimens of factice, whether from coal-tar or petroleum are likely to contain particles of fixed carbon or soot, their absence, proved by solution and filtration, is by no means proof that the bitumen is a true natural asphaltum.

Factice of a very excellent quality, that is stable, tenacious, elastic at two temperatures, and that melts at comparatively high temperatures, that does not contain a trace of coke or soot, is sometimes met with.

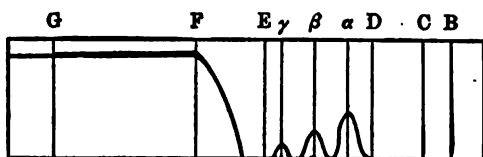


Fig. 7.—Trinidad Asphalt.



Fig. 8.—Alcoholic Solution of 7.



Fig. 9.—Ether Solution of 7.

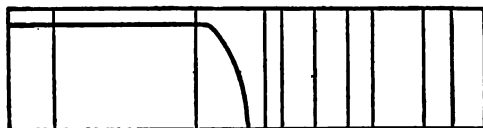


Fig. 10.—Insoluble Residue from 7.

The sulphuric-acid test of Durand-Claye is very valuable. I use 25-c.c. graduated and stoppered jars in which to secure action for 24 hours on 0.1 gm. of the bitumen, by 5 c. c. of fuming sulphuric acid. After standing 24 hours the acid solution is diluted and carefully filtered through a wet filter, into a graduated cylinder and the solution made up with water to 15 c.c. In order to determine the value of the color imparted to the

solution great care should be taken that the different steps in the process shall be as nearly identical as possible. The best means of concentrating the bitumen is by means of an electrical stove set to be heated by the same current. The evaporation should be conducted throughout under as nearly the same conditions as possible. Each of the different steps in the entire process should be duplicated as nearly as possible. Dilution of the solution to 100 c.c. is not necessary, and it

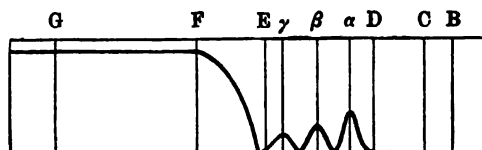


Fig. 11.—Syrian Asphalt.



Fig. 12.—Alcoholic Solution of 11.



Fig. 13.—Ether Solution of 11.

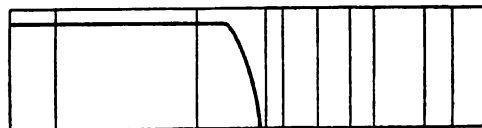


Fig. 14.—Insoluble Residue from 11.

destroys the characteristic shades of color that distinguish the natural asphalts from each other and leaves only the distinction of the highly colored tar-pitches from the light colored natural bitumens. Every one who uses this test should carefully prepare a series of test solutions which should be put in receptacles of colorless glass of uniform diameter. These should be kept in a convenient place for reference and ranged with labels from the darkest to the lightest.

Results obtained by the benzine-alcohol method are good for comparison.

So also is the precipitation method of Kovács and Sötet. Both methods require experience and close observation of minute differences, which with other tests furnish cumulative evidence.

A microscope of low power also furnishes results that are valuable adjuncts to chemical tests. I have found that small fragments of all varieties of bitumen placed on a slide and moistened with a few drops of chloroform furnish characteristic reactions while undergoing solution. The undissolved portions are very peculiar to each species and help, with the other characteristics that must be observed to be recognized, in the determination of any given specimen.

The spectroscope has not yet been found especially valuable, but it has not yet been sufficiently tested to submit to final judgment.

CHAPTER XIV.

MISCELLANEOUS METHODS APPLIED TO STREET MIXTURES AND SURFACES, BITUMINOUS PAVING BLOCKS, BITUMINOUS CONCRETE, WOOD PAVING BLOCKS, CEMENTS, CEMENT MORTARS AND CONCRETES, ETC.

Street mixtures and surfaces, bituminous blocks and concretes are mixtures of a mineral aggregate, pulverized rock or its equivalent, and bituminous mixture of some sort.

The analysis is technical and proximate. It may be partial or complete.

The sample should never be pulverized. Under all conditions and for all purposes, the physical condition of the sample should be changed as little as possible. If the only question to be answered is, simply, what is the percentage by weight that is soluble in carbon bisulphide, nothing is gained by destroying the identity of the mineral residue through pulverizing the sample. When it is desired to learn all that can be learned about a sample, the sample should be broken only sufficiently to secure an average or to put the sample into a wide mouthed flask.

When the sample is a street surface, about 100 gms. should be broken from different parts of the mass, taking care to exclude any binder or fragments of gravel that may have become embedded in the mass. Care should also be taken to secure an average of the mass from top to bottom, as no surface that has been laid longer than a few months is of uniform composition. These fragments should then be rubbed on a flat-bottomed iron mortar. It should not be pounded or rubbed more than is necessary to bring the sample to a uniform coarse powder in which the grains of sand are unbroken. Experience will teach the operator that much may be learned, as to the quality of a surface from its action under the pestle of an iron mortar. Surfaces and mixtures of good quality are never easily broken; they are not only tenacious, but after

being broken, the fragments, whether large or small, readily cohere and again become a solid mass. Poor and dry surfaces and mixtures on the contrary are readily broken and will cohere only slightly if at all. Good surfaces or mixtures do not easily soil the fingers at ordinary room temperatures, while surfaces containing an excess of flux, and those that are too soft are sticky and stain the fingers. These dry surfaces and mixtures rub in the mortar like sugar; while the sticky ones roll into balls and are sometimes greasy, and while not easily reduced to small particles are not strong and tenacious.

Portions of 5 gms. each, are weighed in duplicate into balanced filters, and placed in stoppered funnels. They are then treated precisely as described on page 154 for crude asphalts either with one solvent or more, as is desired.

For ordinary purposes, 100 gms. is a sufficient quantity of the material of an asphalt paving block to use for an analysis. If, however, an examination is to be made of the mineral aggregate, 500 gms., or even 1,000 gms., may be taken for that purpose. The most satisfactory procedure, is to put the material into an Erlenmeyer flask of suitable size, broken as little as is possible. Bisulphide of carbon is filled into the flask with vigorous shaking, after which the solution is allowed to stand several hours or over night. When settled the supernatant liquid is poured off into a second flask, and more CS_2 added to the first flask with agitation. After standing, the solution is again decanted and a third portion of the solvent is poured upon the residue. This third portion is generally found to be sufficient. The residue is dried. The mixed solutions are allowed to stand until subsidence is complete; the liquid decanted; the fine residue rinsed upon a filter and washed with a last portion of CS_2 . The filter is dried, unfolded on to a balance pan, the dried residue swept on to it from the flask, and weighed, with the filter balanced by a second paper in the pan that receives the weights. A good balance, that is sensitive to a tenth of a gram, gives sufficiently accurate results.

The clean and dry mineral aggregate is in excellent condition for examination by sieves or under the microscope.

The solution may be evaporated and the bitumen may be further examined as may be desired.

Bituminous concretes may be treated in the same manner as asphalt paving blocks.

Both asphalt paving blocks and concretes may be treated in large separatory funnels. The solution is tedious as some of the bituminous mixtures filter slowly. The fine mineral aggregate that passes the filter must always be recovered by decantation. The only recommendation for this method is the large size, and consequent unbroken mineral aggregate, that may be received into the open funnels.

The analysis of wood paving blocks is a special problem that has received careful study in the Laboratory of the Commissioners of Accounts of the city of New York. As in other cases the selection and preparation of a sample was found to be of the greatest importance. In all commercial lots of treated wood blocks that we have seen there were a few, to many that were not "thoroughly treated." The external appearance of these blocks was no indication of their interior condition as in all cases the outside was covered with the fluid used for treatment. All of the solvents used to extract this fluid dissolved an appreciable amount of resin and other extractive matters, including water from untreated blocks of yellow pine, and an attempt was made to determine an average amount of this extract. The amount was found to vary to such an extent as to present very wide extremes in any half-dozen blocks taken at random.

While this investigation was in progress a great variety of solvents were used in extracting both the treated and untreated blocks, including petroleum ether, benzole and its homologues, alcohols, bisulphide of carbon, etc. They were all discarded for various reasons and pure acetone was used in their place. This liquid is easily procured, is cheap and is so volatile as to be easily and completely removed from the exhausted residues. The apparatus used consists of the revolving support and separatory funnels described on page 186.

The only way in which samples could be prepared from which duplicate results could be obtained on analysis, was found to be by sawing through the block across the grain of the wood and thoroughly mixing the sawdust. In general, three such cuts through a block gives a fair average of the treatment of the block; but, it is frequently found that, from

blocks that are well treated the sawdust from the three cuts is unlike, while blocks that are indifferently treated furnish very different results from the three cuts.

These remarks apply only to blocks treated with a mixture of rosin and dead oil; from straight coal-tar. Acetone will not dissolve water-gas-tar, and other tars and residual pitches that are often used to saturate wood blocks.

Blocks that are treated with the dense residuum oil, from the distillation of creosote oil, cannot be completely extracted with acetone. Chloroform is the proper solvent for these blocks.

It has been sometimes found necessary to examine the creosote oil used for impregnating wood blocks, and other oils and tars of high boiling points, as well as malthas that are very dense and also of high boiling points, in such a manner as to separate their proximate principles and thus furnish some information respecting their fitness or unfitness for use in impregnating compounds.

The apparatus that experience has shown to be most suitable for this purpose is very simple, and at the same time, must fulfill certain conditions that cannot be overlooked. An 8-ounce (250 c. c.) retort should be selected, of Jena glass, with a bulb as nearly spherical as possible, with a tubular that has no stopper. Into the tubular should be fitted a soft cork. A tightly fitting thermometer stem should pass through the cork, the bulb of which should reach within half an inch of the surface of the liquid that is to be distilled. A cylinder should next be provided of any non-conducting material of about 4-in. internal diameter and 5-in. high. I use a graphite cylinder, but one made of sheet iron and lined with four or five thicknesses of heavy asbestos paper, that can be coiled compactly into a circular lining is just as good. A slot is cut down about $2\frac{1}{2}$ inches deep on one side to receive the neck of the retort. A retort stand is provided with a ring of about the same diameter as the cylinder, over which is spread a piece of coarse wire gauze. Upon this gauze is spread a thin cushion of asbestos fiber, upon which the retort is placed. The charge of about 100 grams is either weighed or measured into the retort, the retort placed in the cylinder, the thermometer stem adjusted, and the

top of the retort lightly covered with asbestos fiber. The thermometer should register above six hundred degrees.

The condenser should be a tube about one centimeter in diameter and about thirty inches long, swelled at one end to receive the neck of the retort. For the purpose for which this apparatus is used it is not necessary to use water as a condenser. The air at the temperature of the room is sufficient. Many of the substances condensed are solid at ordinary temperatures and would plug the tube of an ordinary Liebig's condenser, if completely cooled.

The distillate should be received into small, graduated cylinders, which admit of dividing it into small fractions.

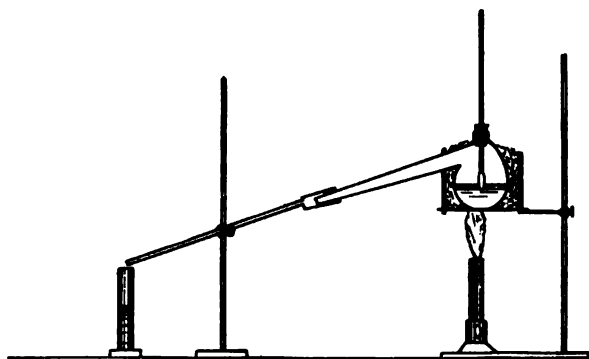


Fig. 15.—Retort and Graphite Hood.

Either a one, three, or six tube Bunsen's burner may be used for heating the charge; ordinary care being exercised to regulate the heat in proportion to the rapidity of the flow.

If it is desired to estimate the distillate in fractions by weight, the fractions may be received into small crystallizing basins that have been tared, and then weighed.

This apparatus will be found very useful in the examination of all bitumens that yield distillates that condense at the temperature of boiling water or above it.

Fig. 15 shows the apparatus in section.

The following is a description of the manner of using the apparatus represented in Fig. 15. One hundred grams are placed in the retort, (either by weight or measure) and are warmed cautiously until the water is expelled, and then heated

until the rate of distillation is about two drops per second. The distillate is collected in tared glass dishes that may be either graduated cylinders or crystallizing basins. Notes are taken of the amount of distillate between

0° and 315° Centigrade.

Above 315° Centigrade.

As the distillation proceeds, after the water has been removed, the phenols come over a little above the boiling point of water; then naphthalene appears as a yellow crystalline solid, that is followed by a greenish yellow solid containing anthracene. The last portion of the distillate is a dark brown oil.

The genuine creosote oil is readily distinguished from the water-gas-tar and other similar residuums that have lately been substituted for it, in the treatment of wood blocks. While the distillate from creosote, or dead oil, is always as above described, the distillates from the tars and residuums contain little or no phenols, naphthalene or anthracene. They consist of a much smaller total percentage of dark brown oils, free or nearly free from solid matter.

The value of these tars and residuums that are practically free from phenols, anthracene and naphthalene has yet to be determined.

Much remains to be learned concerning this subject.

The mineral aggregates are separated by sifting. They may be determined by weight in percentage proportions from the residues on the different sieves. A low power microscope frequently furnishes valuable information and more rarely, a chemical analysis is desirable.

A METHOD FOR A CORRELATION OF THE PHYSICAL AND CHEMICAL EXAMINATION OF CEMENTS, CEMENT MORTARS AND CONCRETES.

Before proceeding to a discussion of the subjects embraced under this title, I would designate several topics that I wish to bring clearly before the reader as neither directly nor indirectly involved in such discussion. It is my intention to discuss a series of technical problems from a purely technical standpoint. These problems relate solely to the use of cements

in mortars and concretes. In the operations or results attending the use of cements it is of no importance whether the lime, silica, alumina and iron are in one manner of combination or another, whether they are in intimate mechanical admixture or "solid solution," no matter how important or interesting these problems may be to the theoretical chemist or to the manufacturer of cement who makes his mixtures to conform to one formula or another. The one who uses cement applies it to certain uses and determines its fitness for such uses by means of certain tests that give him valuable data without any inquiry concerning theoretical problems.

I propose to discuss the determination of a method for a comparative analytical examination of cements, cement mortars and concretes correlative with their properties as revealed by physical tests. A brief review of the most important researches prosecuted in recent years will not only show the lack of any correlation between the chemical and physical examination of cements, but will further show, that no attempt has been made to bring an examination of mortars and concretes into correlation with either the chemical or physical examination of the cements from which they are made.

It is impossible to enumerate here all of the attempts and the results of the attempts, made in the United States and Europe in recent years, to formulate a method of analysis that shall fully satisfy all the parties interested in the analysis of cements. It is only necessary to consult the literature of the subject to discover that such attempts have not been satisfactory. In many instances the want of correlation between the chemical and physical tests are either frankly confessed or are not mentioned. From this multitude of varying propositions, in which, often, the points of difference are more noticeable than those of agreement, I select as most important the reports to the New York section of the Society for Chemical Industry by their sub-Committee on Uniformity of Analysis of Materials for the Portland Cement Industry, and the reports of the special committee on the proper manipulation of tests of cement made to the American Society of Civil Engineers. To properly show the relation of these reports requires a few words of explanation. At a date prior to April, 1900, the American Society of Civil Engineers appointed a special com-

mittee of which Prof. George F. Swain, Prof. of Civil Engineering in the Massachusetts Institute of Technology, was chairman. This committee made a progress report which was published in the Proceedings of the Society, Vol. XXVI, No. 4, April, 1900.

This report consists of the various replies to a long list of questions offered by many persons, and submitted by the chairman of the committee, Prof. G. F. Swain, without comment. From this report is quoted the

Scheme of Prof. Henry Carmichael.—In reply to Question 5 (one of the above-named questions),

What elements of compounds should be determined?

Professor Henry Carmichael of Boston, Mass. (who is an acknowledged authority as a cement expert), says:

"Hydraulic cement consists of a double silicate of lime and alumina (including iron oxide), which is readily soluble in dilute hydrochloric acid, leaving little or no insoluble residue. In addition to the soluble silica and the oxide of calcium, aluminum and iron, good cement contains traces of the oxides of magnesium, sodium and potassium, together with traces of carbonates, sulphates, chlorides and combined water, and finally minute amounts of insoluble sand or cinder."

In reply to Question 6,

"What do you consider the best methods of determining these compounds with sufficient accuracy?"

Prof. Carmichael continues:

"The sample is ground fine in an agate mortar. One gram is carefully weighed out in a shallow porcelain dish and well covered with a 3 per cent solution of hydrochloric acid. After several hours the cement should completely dissolve in this acid with the exception of a small amount of sand, mostly black cinder, from the fuel employed in making the cement. The residue, if any, is filtered off and determined. The clear solution is evaporated to dryness on a water bath in a flat dish. Hydrochloric acid is poured over the dry residue, and the acid is then evaporated. Add a few drops of same acid, again drive off acid. Moisten residue again with same acid and boil up with pure water. The silica is rendered insoluble by the above operation and can be filtered off and weighed. The silica which thus dissolves in the dilute acid, and is in

turn rendered insoluble, is the silica which is available in the setting of the cement. The filtrate from silica is boiled with a few drops of nitric acid, and pure ammonia is then added, which precipitates the oxides of iron and aluminum. With the ammonia is added also ammonium chloride in sufficient quantity to retain the lime in solution. After boiling for some time, the oxides of iron and aluminum are filtered off, and after drying are ignited and weighed."

Here follow directions for separating the iron and aluminum:

"To the filtrate from iron and aluminum oxides is added a slight excess of ammonium oxalate, whereby the lime is precipitated as oxalate which is filtered off, ignited at a dull red heat in a platinum crucible and weighed as carbonate."

His scheme offers further details for the determination of the ingredients that he says are found in good cements in traces; for the determination of water and carbonic acid by ignition; and for the determination of free lime by titration.

I quote further the

Scheme of R. L. Humphrey.—"One-half gram of the finely pulverized sample dried at 100° C., is thoroughly mixed with four or five times its weight of sodium carbonate, and fused in a platinum crucible until CO_2 no longer escapes; the crucible and its contents is placed in a beaker, and twenty or thirty times its quantity of water, and about 10 c. c. of dilute HCl is added; when complete solution is effected, it is transferred to a casserole and placed on a water-bath, and evaporated to dryness several times. The mass is taken up with dilute HCl and water, heated for a short time and filtered thoroughly, washing the residue on the filter with hot water. The filter is dried, ignited and weighed. This weight (less ash) gives the amount of SiO_2 ."

"The filtrate is brought to boiling and ammonium hydrate added in slight excess, the boiling is continued until the odor of ammonia is no longer perceptible. Filter and wash. Redissolve in hot dilute HCl, again precipitate with ammonia and filter through the previous filter and wash with boiling water. The precipitate dried, ignited and weighed, less ash, gives the amount of Al_2O_3 and Fe_2O_3 ."

Then follows a method of separating iron from alumina:

"The filtrate from the iron and alumina is heated to boiling, and boiling ammonium oxalate is added until a precipitate is no longer formed. After boiling for a few minutes, it is set aside for a short time; when the precipitate has settled perfectly, decant the clear liquid through a filter, wash by decantation, dissolve the precipitate in hot dilute HCl, using as small a quantity as possible to effect a complete solution; heat to boiling and add ammonia; heat on a water-bath for a few minutes; when the solution clears, filter through the previous filter, wash thoroughly with hot water. Dry the precipitate, ignite to constant weight, and weigh as CaO, or determine the lime volumetrically by titration with potassium permanganate."

He then determines the ingredients occurring in small proportion. He determines SO_3 in a separate portion after removing the silica.

In the Journal of the Society of Chemical Industry for January 15, 1902, page 12, will be found the report of the sub-Committee on Uniformity in Analysis of materials for the Portland Cement Industry. This committee consisted of Clifford Richardson, S. B. Newberry and H. A. Shaffer. They sent out a circular asking the chemists addressed to join them in analyzing samples of raw cement mixture and finished Portland cement, "sending your results and a description in detail of your methods of analysis * * *. From comparison of the results and methods which are recorded it is hoped that some uniform method can be arranged which can be relied on for general use so that such discordant results as have been obtained at times in the past may be avoided." To this circular eighteen chemists responded of whom thirteen were chemists to manufacturers of Portland cement, one was one of the chemists to the Geological Survey at Washington, Dr. Hillebrand, and the other four sustained relations to the subject unknown to us.

The results obtained by these gentlemen were very various and their methods were equally so. One used a general method for rock analysis, which was of course ultimate. Seven fused the assay; four powdered it; two dried it; three dissolved it in dilute acid; six dissolved it in strong acid, while

only two specifically stated that they treated the sample of cement as it was received.

After reviewing these various methods and results Dr. Hillebrand reaches the following conclusions:

Dr. Hillebrand's Conclusions.—"The chief conclusions derived from a critical examination of all the data reported are embodied in the following summary of rules, and they bear out fully the views long since formed and frequently published by myself.

"To the non-observance of these rules, coupled with incomplete washing, of precipitation, and perhaps in some cases the employment of impure reagents are to be attributed nearly every one of the more or less marked variations in the tabulated analyses.

"(1) Cement samples whose composition is to be controlled by different chemists should be sealed air-tight and not opened until the analysis is about to be made.

"(2) Mode of Attack.—Limestone and raw cement mixtures should be heated over the blast in order to render them wholly soluble and to oxidize sulphides and organic matter. If any residue should remain on treatment with hydrochloric acid (with finished cements as well) this should be collected without evaporation and fused with a minimum of sodium carbonate, its hydrochloric solution being added to the former.

"For sulphur an oxidizing attack, either in the wet or dry way, must be used with both limestone and cement in order to obtain all the sulphur.

"(3) Separations.—(a) Without two alternating evaporations and filtrations it is impossible to obtain a correct result for silica, no matter how or at what temperature dehydration has been conducted. The blast should always be applied for at least ten minutes, and in careful work correction by hydrofluoric and sulphuric acids should not be neglected.

"(b) Iron and aluminum, with any titanium and phosphorus present, should be twice precipitated by ammonia in presence of sufficient ammonium chloride to retain magnesium in solution. Without this double treatment very appreciable amounts of lime will contaminate the alumina. If manganese is present in more than traces it is advisable to add bromine before the ammonia, so as to weigh most of the manganese

with the alumina rather than with the lime and magnesia. Application of the blast is advisable.

"(c) Iron cannot be accurately determined volumetrically or by weight, in presence of titanium if zinc is employed for its reduction. Hydrogen sulphide should be used and all excess boiled out in a current of carbon dioxide.

"(d) In accurate work lime should be twice precipitated, whether it is to be determined volumetrically or by weight, and at least one hour should intervene between precipitation and filtration. Compensation of errors affords satisfactory results in the hands of few operators with but a single separation from magnesium.

"(e) Magnesium pyrophosphate is only to be obtained of normal composition after long blasting (Neubauer), when precipitated under the conditions prevailing in technical analysis, that is, in presence of much ammonia and ammoniacal salts, especially the oxalate.

"Strict observance of all the above rules is doubtless often impossible in the hurried routine of a technical laboratory, but the inevitable penalty of material deviation from them is a decrease in the accuracy of the results."

Dr. Hillebrand then offered some "Suggestions regarding Scheme of Analysis submitted by Mr. Clifford Richardson," as follows:

Dr. Hillebrand's Suggestions.—"The title should cover analysis of limestones and limestone mixtures as well as finished cements.

"Paragraph 1 should prescribe the ignition of limestone and raw mixtures and the fusion of any residue (from cements also) that may be insoluble in hydrochloric acid with a small amount of sodium carbonate, and the addition of the hydrochloric acid solution of this fusion to the former. From this point the procedure should be identical in both cases.

"SiO₂. The time of blasting silica can be very well shortened to a maximum of 10 minutes, without further check, when but ½ gm. of sample is operated on. The weight of silica will rarely exceed 1 decigram and 10 minutes should suffice for its complete dehydration over a good blast.

"The strength of HCl solution used in the silica evaporation should be stated approximately. I should call 5 c. c. of

acid of 1.12 sp. gr. much too little to use, for it would only contain about 1 gm. of HCl. It should be made clear that the evaporated residue is to be digested with the acid a little while before further diluting.

"Al₂O₃, etc. It is perhaps hardly necessary for a technical analysis to prescribe that the precipitate shall be dried and removed from the filter, though this might be recommended for the best work.

"Fe₂O₃. The H₂S method of reduction should be prescribed for the best work.

"FeO. For technical work it does not seem necessary to prescribe any rule for FeO.

"CaO. The time allowed for settling the first CaC₂O₄ precipitate (2 hours) is quite too much if a second precipitation and filtration are to be made the same afternoon. The time schedule is in error on this point. The "outline" makes it appear that the full flame is applied at once to the moist CaC₂O₄ precipitate wrapped in its paper. I know that this is done by some European chemists with ammonium magnesium phosphate, but I should question its advisability here.

"Blasting for 10 to 15 minutes without any further check ought to be sufficient to reduce the CaO. Personally I never find more than 5 to 10 minutes' blasting necessary. I do not insist on this point, but offer it in interest of time saving.

"MgO. After the precipitate has formed I should add more than three or four drops of ammonia to hasten complete precipitation. With all the ammonium salts present I regard it as useless to follow strictly the directions of Gibbs, Gooch and Austen, for precipitating Mg, and would rely on long blasting to secure normal Mg₂P₂O₇. It should be stated that dilute ammonia water is used for washing.

"When a Gooch crucible is used I should hesitate to recommend the blast, at least unless it is well known that the asbestos undergoes no change at this high temperature. Some asbestos which stands the Bunsen flame will not endure that of the blast.

"SO₃ and S. To save time I should omit the evaporation of silica to dryness. It is an unnecessary precaution. I presume total sulphur can be obtained by a wet oxidation as well as a dry one. If the latter is used the crucible should be set in

a hole in asbestos board to keep out sulphur from the gas flame. It is just as well to nearly neutralize with ammonia before adding barium chloride.

"H₂O. Not necessary to mention Penfield's method, which is only safe in careful hands, especially when any CO₂ or sulphides are present."

Mr. Clifford Richardson's Scheme for Analysis.—These suggestions were followed by "a tentative method suggested by Mr. Clifford Richardson, for the analysis of limestone, raw mixture and Portland cement, proposed for trial by the committee and modified in accordance with the suggestions of W. F. Hillebrand."

"Solution. One-half gram of the finely powdered substance is to be weighed out, and if a limestone or unburned mixture, strongly ignited in a platinum crucible over the blast for 15 minutes. It is then transferred to an evaporating dish, preferably of platinum for celerity in evaporation, covered with a watch glass and 10 c. c. of HCl diluted with about 50 c. c. of water, added. Digestion on the water-bath is allowed to go on for about 15 minutes when the substance should be entirely decomposed.* The cover glass is then removed, washed and evaporated to dryness, as far as this may be possible on the bath.

"Silica. The residue without further heating, is treated at first with 5-10 c. c. of strong HCl, and then with as much water as the dish will comfortably hold. The cover is then replaced and digestion allowed to go on for 10 minutes on the bath, after which the solution is filtered and the separated silica washed thoroughly with hot water. The filtrate is again evaporated to dryness, the residue, without further heating, taken up with acid and water and the small amount of silica it contains separated on another filter paper. The papers containing the residue are transferred wet to a weighed platinum crucible, dried, ignited, first over a Bunsen burner until the carbon of the filter is completely consumed, and finally over the blast for 30 minutes and checked by a further blasting of 10 minutes or to constant weight. The silica, if great accuracy is desired, is treated in the crucible with about 10 c. c. of HF

*If anything remains undecomposed it should be separated, fused with a little Na₂CO₃, dissolved and added to the original solution.

and four drops of H_2SO_4 , and evaporated over a low flame to complete dryness. The small residue is washed, finally blasted, cooled and weighed. The difference between this weight and the weight previously obtained gives the amount of silica.*

" Al_2O_3 and Fe_2O_3 . The filtrate, about 250 c. c., from the second evaporation for SiO_2 , is made alkaline with NH_4OH and boiled, to expel excess of NH_3 , or until there is but a faint odor of it, and the precipitated iron and aluminum hydrates, after settling, are washed once by decantation and slightly on the filter. Setting aside the filtrate, the precipitate is dissolved in hot dilute HCl , the solution passing into the beaker in which the precipitation was made. The aluminum and iron are then reprecipitated by NH_4OH . The second precipitate is collected and washed on the same filter used in the first instance. The filter paper, with the precipitate, is then placed in a weighed platinum crucible, the paper burned off and the precipitate ignited and finally blasted 10 minutes, with care to prevent reduction, cooled and weighed as $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$.†

" Fe_2O_3 . The combined iron and aluminum oxides are fused in a platinum crucible at a very low temperature with about 10 gms. of KHSO_4 , the melt taken up with hot water and 25 c. c. of dilute H_2SO_4 . The clear solution is then digested on the steam-bath for about 10 minutes, and, if accuracy is desired, the small amount of silica is filtered out, weighed, and corrected by HF and H_2SO_4 . The filtrate is reduced by hydrogen sulphide, boiling out the excess afterwards while passing CO_2 through the flask, and titrated with permanganate.‡

" CaO . To the combined filtrate from the $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ precipitate a few drops of NH_4OH are added, and the solution brought to boiling. To the boiling solution 10 c. c. of a saturated solution of ammonium oxalate is added and the boiling continued until the precipitated CaC_2O_4 assumes a well defined granular form. It is allowed to stand for 20 minutes, or until the precipitate has settled and is then filtered. The precipitate and filter are placed wet in a platinum crucible and the paper

*For ordinary control work in the plant laboratory, this correction may, perhaps, be neglected; the double evaporation never.

†This precipitate contains TiO_2 , P_2O_5 and MnO .

‡In this way only is the influence of titanium to be avoided, and a correct result obtained for iron.

burned off over a small flame of a Bunsen burner. It is then ignited, redissolved in HCl and the solution made up to about 100 c. c. with water. Ammonia is added in slight excess, and the liquid is boiled. The small amount of Al_2O_3 is filtered out, weighed and the amount added to that found in the first determination, when great accuracy is desired. The lime is then reprecipitated by ammonium oxalate, allowed to stand until settled, washed,* weighed as oxide by ignition and blasting to constant weight, or determined with standard permanganate.†.

"MgO. The combined filtrate from the calcium precipitates are acidified with HCl and concentrated on the steam-bath to about 150 c. c., 30 c. c. of a saturated solution of $\text{Na}(\text{NH}_4)\text{HPO}_4$ are added, and the solution transferred to a beaker and boiled for several minutes. It is then removed from the flame and cooled by placing the beaker in ice water. After cooling, NH_4OH is added drop by drop with constant stirring until the crystalline ammonium-magnesium orthophosphate beginning to form and then in slight excess, the stirring being continued for several minutes. It is then set aside for several hours in a cool atmosphere and filtered. The precipitate is redissolved in hot HCl; the solution made up to about 100 cc., 2 cc. of a saturated solution of $\text{Na}(\text{NH}_4)\text{HPO}_4$ added and ammonia, drop by drop, with constant stirring until the precipitate is again formed as described. It is then allowed to stand for about two hours, when it is filtered on paper or a Gooch crucible, cooled and weighed as MgP_2O_7 .

" K_2O and Na_2O . For the determination of the alkalies, the well known method of Prof. J. Lawrence Smith is to be followed, either with or without the addition of CaCO_3 with the NH_4Cl .

" SO_3 . One gram of the cement is dissolved in 15 cc. of HCl, filtered and the residue washed thoroughly.‡

"The solution is made up to 250 cc. in a beaker and boiled. To the boiling solution 10 cc. of a saturated solution of BaCl_2

*The volume of wash water should not be too large, Vide Hillebrand.

†The accuracy of this method admits of criticism, but its convenience and rapidity demand its insertion.

‡Evaporation to dryness is unnecessary. Vide Hillebrand.

is added slowly, drop by drop, from a pipette and the boiling continued until the precipitate is well formed. It is then set aside over night, filtered, ignited and weighed as BaSO_4 .

"Total Sulphur. One gram of material is weighed out in a large platinum crucible and fused with Na_2CO_3 and a little KNO_3 , being careful to avoid contamination from sulphur in the gases from the source of heat. The melt is treated in the crucible with boiling water and the liquid poured into a tall, narrow beaker and more hot water added until the mass is all dissolved. The solution is then filtered. The filtrate contained in a No. 4 beaker is to be acidulated with HCl and make up to about 250 cc. with distilled water, boiled, the sulphur precipitated as BaSO_4 and allowed to stand over night.

"Loss on Ignition. Half a gram of the cement is to be weighed out in a platinum crucible, and blasted 15 minutes. The loss by weight, which is checked by a second blasting of 5 minutes, is the loss on ignition."

At the annual meeting of the American Society of Civil Engineers held January 21, 1903, the special committee on uniform tests of cement made the following progress report:

Chemical Analysis.—"5. Significance.—Chemical analysis may render valuable service in the detection of adulteration of cement with considerable amounts of inert material, such as slag or ground limestone. It is of use, in determining whether certain constituents, believed to be harmful when in excess of a certain percentage, as magnesia and sulphuric anhydride, are present in inadmissible proportions. While not recommending a definite limit for these impurities, the committee would suggest that the most recent and reliable evidence appears to indicate that magnesia to the amount of 5 per cent and sulphuric acid to the amount of 1.75 per cent may safely be considered harmless.

"6. The determination of the principal constituents of cement, silica, alumina, iron oxide and lime, is not conclusive as an indication of quality. Faulty character of cement results more frequently from imperfect proportion of the raw material or defective burning than from incorrect proportions of the constituents. Cement made from very finely-ground material, and thoroughly burned, may contain much more lime

than the amount usually present and still be perfectly sound. On the other hand, cements low in lime may, on account of careless preparation of the raw material, be of dangerous character. Further, the ash of the fuel used in burning may so greatly modify the composition of the product as largely to destroy the significance of the results of analysis.

"7. Method.—As a method to be followed for the analysis of cement, that proposed by the committee on uniformity in the Analysis of Materials for the Portland Cement Industry, of the New York Section of the Society of Chemical Industry, and published in the Journal of the Society for January 15, 1902, is recommended." (See page 221.)

Mr. Bertram Blount's Critique of Mr. Richardson's Report.—In May, 1902, Mr. Bertram Blount of London, England, an eminent English cement expert, read a paper before the New York Section of the Society of Chemical Industry, in which he "demurred to the methods of the committee on two chief grounds: (a) That standardization of strictly analytical processes was undesirable; and (b) that the methods proposed by the committee were erroneous."

In the Journal of the American Chemical Society for August, 1904, Mr. Blount further discusses the work of Dr. Hillebrand and shows that while he finds Dr. Hillebrand and himself nearly in accord "there remain a few matters of great moment to the manufacturers and users of Portland cement and to the chemists who control the quality of their output, which are still in doubt; as the question affects a large industry and is of much analytical interest it may be usefully discussed in detail. . . . One of the principal questions as to the proper method of analyzing portland cement is that of the determination of its insoluble residue. . . . The determination of insoluble residue is of value because the figure obtained is an index of the care which has been used in manufacture; a cement containing 5 per cent of added sand would be diluted to that extent only, whereas one containing 5 per cent of insoluble residue is not merely diluted, but has incontestably been badly made. The method which I devised and have used for nearly twenty years, consists in dissolving the cement in hydrochloric acid, evaporating the solution to dryness, but not intentionally baking the evaporated material, redissolving

in hydrochloric acid, filtering, washing, dissolving out the precipitated silica with sodium carbonate solution and collecting the final insoluble residue. It may be fairly assumed that a siliceous residue which has resisted this series of treatments is inert and valueless as a cementitious material. I believe I am not misinterpreting Dr. Hillebrand when I say that he agrees with this; but he goes further and suggests that the treatment is too drastic and that it would be better to determine the insoluble residue in such a way that it is not exposed to digestion with strong hydrochloric acid. The method he proposes is to dissolve in dilute hydrochloric acid, filter at once and to remove any precipitated silica by means of sodium carbonate. This suggestion is important and has been examined in the following manner. Four samples of cement were chosen and the insoluble residue determined in each, both by the method which Dr. Hillebrand has proposed and that which I ordinarily use."

	Dr. Hillebrand.		Bertram Blount.	
	Per cent.	Per cent.	Per cent.	Per cent.
1	3.48	3.28	1.10	1.16
2	3.34	3.12	1.60	1.64
3	5.20	5.00	1.28	1.36
4	0.80	0.96	0.50	0.54

"If we assume with Dr. Hillebrand that the insoluble residue obtained by his method is inert, evidently the determination of this material is of even greater importance than had been supposed; it is, however, not easy to obtain conclusive evidence on this point. The state of subdivision of the particles comprising cement has a great influence on their activity; unground clinker is scarcely more cementitious than so much limestone. Moderately fine particles, on the other hand, though setting slowly, will set eventually and it would be rash to assume that a material, apparently inert when tested for the short period of time generally available in laboratory experiments, will not prove itself active at long dates, and in practice contribute to the strength of the concrete or mortar prepared with it. Bearing this in mind, one is not surprised to find that the insoluble residue obtained by Dr. Hillebrand's method is a cementitious material. This fact was ascertained in the following way: The insoluble matter from cement No.

1, isolated strictly according to Dr. Hillebrand's prescription, was finally ground and then treated again by Dr. Hillebrand's own method. The final insoluble residue thus obtained was 1.52 per cent and 1.66 per cent in duplicate experiments, as against a previous mean value of 3.38 per cent on the unground substance. In point of fact the retreatment reduces the insoluble residue to something closely approaching that found by my method of analysis, which, on the same cement, gave 1.10 per cent and 1.16 per cent insoluble residue. It would appear from this that the chief difference between the two methods arises from the necessity of more finely grinding the cement if dilute acid is to be used; when fine grinding is substituted for the use of strong acid, similar results are obtained. . . . I thought it possible that this insoluble matter might be cementitious. Accordingly a fairly large quantity (about 25 gms.) was isolated. This was ground and gauged with water after the manner of a cement. As might be predicted, it set feebly; it is, in fact, not a cement per se, but rather a pozzuolanic material. Its activity as a pozzuolana was proved by gaging it with one-third of its weight of quicklime; it set to a hard mass. As there is always an abundant quantity of lime set free from the decomposition of calcium silicate and aluminates in the process of the setting of cement, capable of acting with a pozzuolanic material, I conclude that the insoluble matter, isolated by Dr. Hillebrand's method is not inert, but belongs to the cement itself. The insoluble residue isolated by my own method is almost wholly silica in rather coarse fragments and is substantially inert. On these grounds I prefer my original method for determining insoluble residue."

"Next, with regard to the determination of silica in cement, Dr. Hillebrand has done excellent service in promoting accuracy in mineral analysis by insisting on the necessity of double evaporation. I agree that this double evaporation is necessary when the silica is set free in a mass of material such as is produced when a silicate is fused with sodium carbonate and the melt is decomposed with hydrochloric acid, but I consider it is not requisite when the total quantity of material is small and the whole is well baked. It is perfectly

practicable to obtain substantially the whole of the silica from Portland cement by a single evaporation."

"The next matter in which there is a difference of view between Dr. Hillebrand and myself (Mr. Blount) is where the silica, separated by the ordinary process of solution and evaporation, is pure or contains entangled in or associated with it sensible quantities of alumina and other bases." From Mr. Blount's experience he concludes that the silica is practically pure. He further concludes "that the amount of silica contained in the ammonia precipitate from cement, analyzed in the customary manner, and with only one evaporation for silica, is negligibly small."

And further that, "Experiment has shown that in the analysis of cement, silica can be separated by a single evaporation with a maximum error of 0.32 per cent, and that this error is usually smaller; that the amount of silica appearing with the ferric oxide and alumina will not exceed 0.14 per cent, and is generally less; that a single precipitation suffices for the separation of ferric oxide and alumina from lime and of lime from Magnesia."

In the November, 1904, number of the Chemical Engineer appears a

**METHOD FOR ANALYSIS OF PORTLAND CEMENT
AND CEMENT MATERIALS RECOMMENDED BY
THE COMMITTEE OF THE LEHIGH VALLEY
SECTION OF THE AMERICAN CHEMICAL SOCIETY.**

Cement.—"Pass the sample through a 100-mesh sieve to free it from clinkers and foreign matter, and keep in a stoppered bottle. Weigh out 0.5 gm. into a wide platinum dish of about 50 cc. capacity: add a very little water and break up lumps with a glass rod; add 5 cc. hydrochloric acid (1-1) and evaporate to dryness at a moderate heat, continuing to heat the mass—not above 200° C—until all odor of acid is gone. Do not hurry this baking or skimp the time. The whole success of the analysis depends on thoroughness at this point. Cool; add 20 cc. hydrochloric acid (1-1); cover, and boil gently for ten minutes; add 30 cc. of water, raise to boiling,

and filter off the silica ; wash with hot water four or five times ; put in crucible, ignite (using blast for ten minutes) and weigh as SiO_2 ."

The treatment of the solution follows with essentially little difference, between this scheme and those which have preceded it.

The above committee, consisting of W. B. Newberry, R. K. Meade and E. B. McCready, prepared a circular letter which was sent to thirty chemists of Portland cement works and from their replies as well as from the investigations of individual members of the committee the method was recommended.

Now it is quite clear that the problems presented to a chemist in a cement manufactory, and the problems presented in a city laboratory, and the problems presented to Dr. Hillebrand, are wholly different, and require for their solution consideration of wholly different methods of procedure. The problems presented to Dr. Hillebrand were wholly scientific and have been treated by him in a manner that leaves nothing to be desired. While the strictly scientific aspects of the subject have been discussed in a masterly and well-nigh exhaustive manner, resulting in the presentation of a large amount of analytical data of the greatest value, the questions have been left wholly undetermined whether or no ultimate methods of analysis are to be applied indiscriminately to the solution of the three classes of problems mentioned above ; or, if proximate methods are preferable, in what cases are they preferable ? Those engaged in the manufacture of cement can best decide what method of analysis will best solve the problems presented to them. So, too, those who use cement and those who control the use of cement can best decide what methods are best suited to the time, place, conditions and identity of the problems presented to them for solution.

There are a multitude of reasons, too numerous to mention, why the judgment of Mr. Blount is sound, that each chemist should be left free to decide for himself what analytical methods he will use, for if the analyst is not capable of making this decision, he is like a general in the field subject to the dictation of a bureau.

We have brought together here the most valuable attempts that have been made within the last eight years to bring before the chemists of the country a method of analysis that they may all be expected to follow. It is to be presumed that as a motive therefor, each of the authors of these several schemes was prompted in his work by some ultimate purpose. An examination of the schemes show an essential likeness in the treatment of the solutions in hydrochloric acid that are obtained, and at the same time that the methods used in obtaining these solutions are in no two cases alike, hence it is fairly inferred that the motives that prompted the schemes are as unlike as the schemes themselves.

Referring to the scheme of Prof. Henry Carmichael (page 219), he says:

"The sample is ground fine in an agate mortar. One gram is carefully weighed out in a shallow porcelain dish and well covered with a 3 per cent solution of hydrochloric acid. After several hours the cement should completely dissolve in this acid with the exception of a small mount of sand, mostly black cinder, from the fuel employed in making the cement. The residue, if any, is filtered off and determined.

"The clear solution is evaporated to dryness on a water bath in a flat dish. Hydrochloric acid is poured over the dry residue, and the acid is then evaporated. Add a few drops of same acid, again drive off acid. Moisten residue again with same acid and boil up with pure water. The silica is rendered insoluble by the above operation and can be filtered off and weighed. The silica which thus dissolves in the dilute acid, and is in turn rendered insoluble, is the silica which is available in the setting of the cement.

Mr. R. L. Humphrey (page 220) says:

"One-half gram of the finely pulverized sample dried at 100° C., is thoroughly mixed with four or five times its weight of sodium carbonate, and fused in a platinum crucible until CO₂ no longer escapes; the crucible and its contents is placed in a beaker, and twenty or thirty times its quantity of water, and about 10 cc. of dilute HCl is added; when complete solution is effected, it is transferred to a casserole and placed on a water bath, and evaporated to dryness several times. The mass is taken up with dilute HCl and water, heated for a short

time and filtered, washing the residue on the filter thoroughly with hot water. The filter is dried, ignited and weighed. The weight (less the ash) gives the amount SiO_2 ."

Dr. Hillebrand (page 222) says:

"Mode of Attack.—Limestone and raw cement mixtures should be heated over the blast in order to render them wholly soluble and to oxidize sulphides and organic matter. If any residue should then remain on treatment with hydrochloric acid (with finished cements as well) this should be collected without evaporation and fused with a minimum of sodium carbonate, its hydrochloric acid solution being added to the former."

Mr. Richardson, for his committee (page 225) says:

"Solution.—One-half gram of the finely powdered substance is to be weighed out and, if a limestone or unburned mixture, strongly ignited over the blast for 15 minutes. It is then transferred to an evaporating dish . . . and 10 cc. of HCl diluted with about 50 cc. of water, added. Digestion on the water bath is allowed to go on for about 15 minutes when the substance should be entirely decomposed." He adds in a note, "If anything remains undecomposed it should be separated, fused with a little Na_2CO_3 , dissolved and added to the original solution."

Mr. Bertram Blount (page 229) says:

"The method which I devised and have used for nearly twenty years, consists in dissolving the cement in hydrochloric acid, evaporating the solution to dryness, but not intentionally baking the evaporated material, re-dissolving in hydrochloric acid, filtering, washing, dissolving out the precipitated silica with sodium carbonate solution, and collecting the final insoluble residue. It may be fairly assumed that a siliceous residue which has resisted this series of treatments is inert and valueless as a cementitious material."

Finally, we have the method "recommended by the committee of the Lehigh Valley section of the American Chemical Society" (page 232). The committee says:

"Pass the sample through a 100-mesh sieve to free it from clinker and foreign matter and keep in a stoppered bottle. Weigh out 0.5 gm. into a wide platinum dish of about 50 cc.

capacity; add a very little water and break up lumps with a glass rod; add 5 c. c. hydrochloric acid (1-1) and evaporate to dryness at a moderate heat, continuing to heat the mass—not above 200° C.—until all odor of acid is gone. . . . Cool; add 20 cc. hydrochloric acid (1-1); cover and boil gently for two minutes; add 30 cc. of water, raise to boiling and filter off the silica; wash with hot water four or five times, put in crucible, ignite . . . and weigh as SiO_2 .”

How can uniformity of results be expected to be obtained by the use of six fundamentally different methods? These schemes are designed for the manufacture of cement to exhibit the ultimate composition of cements. They are in no sense technical. They offer no opportunity for comparative results, hence they are of no value in our discussion. We shall, however, use them as examples to enforce certain conclusions to which we have been led.

In addition to these schemes, we wish to call attention to correspondence which we have held with a prominent manufacturer of cement, in which he indulged in the following criticisms:

“Experiments we have made show that the solubility of commercial portland cements in dilute acid depends greatly upon the fineness of grinding.

“We have found no cements which if ground to extreme fineness in an agate mortar, show more than a fraction of 1 per cent of insoluble matter.

“Since even the monosilicate of lime, Wollastonite, is readily decomposed by acid, it is evident that the residue should contain practically no lime, and would consist of a minute amount of uncombined clay.

“It is impossible that this should reach more than a fraction of 1 per cent in a good cement.

“Would say further that the use of sufficiently dilute acid and fine grinding will give a clear solution without any separation of gelatinous silica.

To which we replied:

The first sentence of your letter furnished a key to the whole matter. You say:

“That experiments we have made show that the solubility

of commercial Portland cements in acid depends greatly upon the fineness of grinding."

Believing that this fact as stated by you has been proved beyond any question, I insist that every sample of cement shall be analyzed in exactly the condition in which it is brought to the laboratory; that is, that the specimen shall be neither dried nor pulverized, nor in any manner treated in such a way as to either lessen or increase the differences that exist between the samples as they are brought upon the works or are subjected to physical tests.

I have not yet found a ponderable amount of lime in any of the residues from dilute acid that I have examined.

If you would advocate the uniform grinding of samples of cement to an impalpable powder, in an agate mortar, in order that they may be more completely dissolved and brought into solution, I insist that I do not agree with you.

I believe that cement of proper fineness for use is soluble in 10 per cent hydrochloric acid ($1\text{HCl. sp. gr. } 1.2 \text{ to } 9\text{H}_2\text{O}$), without gelatinization, and that any matter not so soluble, contained in commercial cement, is not cement at all, and is, and should be classed as "inert matter."

To which he replied:

"Your separation of the constituents of cement by the action of 10 per cent hydrochloric acid on the commercial cements, appears to me to be without foundation.

"The varying amounts of insoluble matter obtained by you on treating the same cement with acid of varying strengths and in various ways appears to show that the amount of insoluble matter depends upon the method employed, rather than upon the chemical character of the cement analyzed.

"I have found that most commercial Portland cements, if ground to great fineness, give scarcely any insoluble residue on treatment with sufficient quantity of 5 per cent acid.

"The high percentage of insoluble matter obtained by you simply results from the comparatively coarse grinding of the cement.

"You certainly will not contend that the composition of the coarser particles is materially different from that of the fine ones, or that the chemical character of the cement is

changed by grinding the coarse particles to uniform fineness with the rest.

"Your choice of 10 per cent acid and method of mixing appear to me to be wholly arbitrary, and the conclusion drawn from the amount of insoluble matter obtained to be quite unjustified.

"Since coarsely ground cement gives a considerable residue when treated with dilute acid, while finely ground cement gives practically none, and since this residue consists chiefly of silica, and contains, as stated by you, practically no lime, it appears to me evident that this insoluble matter results chiefly from local separation of silica contained in the coarse particles.

"The lime and other constituents contained in these particles, are, however, dissolved, and are included by you in the group of active constituents.

"The injustice of this is apparent.

"If the silica of the coarse particles is inactive, the lime must be so also.

"It is undoubtedly correct to submit commercial samples of cement to physical tests as they are received, without grinding.

"To submit these samples to chemical analysis, however, without bringing them into homogeneous condition by grinding, is certain to lead to erroneous conclusions.

"In burning, however, a disturbing factor enters, and this is the ash of the coal dust used as fuel.

"This ash adds at least 2 per cent to the silica, alumina and iron oxide of the product.

"It is, however, brought into combination with the lime of the charge sufficiently to become wholly soluble in acid, but not uniformly enough to allow the lime of the raw material to be raised to a corresponding extent.

"I believe fully that the best Portland cements are thoroughly homogeneous in character, and that the excess of silica, alumina and iron over that called for by the formula is due to the ash of the fuel and to the general practice of carrying the lime a little below the maximum in order to offset possible fluctuations in the mixture."

I asked my correspondent to send me a sample of the fuel ash.

He replied:

"It will be impossible to send you a sample of the coal ash to which you refer, as this melts in with the clinker with which it comes in contact in the rotary kilns.

"The amount of fuel used is about 150 lbs. to the barrel of cement.

"The ash of this fuel is about 8 per cent, and if all absorbed by the clinker would add about 3 per cent of silica, iron and alumina to the latter."

The absolute worthlessness of an ultimate analysis of cements, cement mortar and concretes was forcibly brought to my attention at the outset of my investigation of this subject. No one disputes that a cement that has not been damaged by exposure is brought upon the works and is made into mortar and concrete, substantially, just as it leaves the manufactory. In this condition it is subjected to physical tests. The fineness of its grinding is one of the properties that materially affects the results of physical tests. These tests are also, to some extent, determined by the amount and kind of material that is not cement that is accidentally, carelessly or purposely mingled with the cement, or that results from the inevitable defects of a technical process of manufacture that is only approximately perfect.

No one who was about to apply physical tests to a sample of cement brought from work in progress, would sift the sample through a 100-mesh sieve to remove "clinker and foreign matter," nor would he pulverize it to improve its cohesive strength, nor dry it to remove water that may have been absorbed. The cement goes into the mortar and concrete as it is received upon the work in progress, with all of the sand, ashes, unburned slurry, over-burned slurry, unburned cement rock and other "foreign matter" that it may contain, and with all the imperfections of grinding; in fact, with all the qualities good and bad, which it may possess. To attempt to remedy or supplement any defects possessed by the sample before applying the physical tests would make those tests a farce as a means of determining the qualities of the cement in actual use. Why is it any less a farce to conduct a chemical examination

in such a manner as to improve the qualities of the sample by supplementary grinding or by sifting out the "clinker and foreign matter;" or by adding the silica of the sand and ashes to the silica of the cement by fusion with Na_2CO_3 , or by the action of concentrated HCl ; or, by the same means adding the alumina and iron of the ashes to the alumina and iron of the cement. To expect correlation under such conditions is the most complete unreason.

The requirements of the problem demand that whereas, the same substance as it leaves the manufactory is made into mortar and concrete and is subjected to physical tests, the same substance shall be subjected to chemical tests and in such manner that the identity of the substance shall not be lost or subjected to change at any step in the progress of such tests.

In the determination of what this manner shall be the question arises, "What is cement," from a technical standpoint? The question is answered, it is a pulverized material that when mixed with water under certain conditions develops hydraulic properties and cohesive strength. The primary consideration is, permanent cohesive strength when mixed with sand as mortar and with sand and stone as concrete.

The constitution of cements has been under discussion for many years, but no results approaching finality may be said to have been reached until those described by the Messrs. Newberry were published in 1897. It is not necessary here to review the work of Le Chatelier and Vicat. That work has been sufficiently well done by the Messrs. Newberry in their several papers. I wish, however, to re-state the Newberry's results in order to point out their relation to the present work.

The Newberrys have shown, by the most elaborate and conclusive physical and chemical tests, that the formula for cements is " $\% \text{ lime} = 2.8 (\% \text{ silica}) + 1.1 (\% \text{ alumina})$." They have further shown that in the manufacture of cement, alumina and iron may be taken together, while magnesia is inert, and sulphuric oxide and the alkalis in small quantity may be disregarded. From all of which it is fair to conclude that the lime, soluble silica, iron and alumina are the constitu-

ents of a cement that give it value, while all the other constituents that it may contain are inert or injurious.

It may therefore be assumed that a perfect theoretical cement, formed synthetically from pure materials, would be found upon analysis to be represented by the formula

Ca

= 1

2.8 Soluble Silica + 1.1 Alumina and Iron Oxides

No cement, either Portland or Rosendale or slag, on the market, consists of chemically pure hydraulic cement. A commercial Portland cement therefore consists of the above-named compound, plus, not a trace, but an unavoidable percentage of the ashes of the coal employed as fuel, also of over-burned and under-burned clinker, also of uncombined clay, magnesia, sulphuric oxide, alkalies, water and carbonic oxide (CO_2). In cements of good quality those percentages are small; but in cements that are poorly prepared or purposely adulterated they are varyingly larger.

In the case of natural cements, there is in addition to those above mentioned, an unavoidable percentage of both over-burned and under-burned cement rock, particularly the latter, together with more or less minute fragments of the fuel used that are ground up with the cement.

It is assumed that these impurities are unavoidable, because from the nature of the case no cement can be manufactured without some of them and no cement that I have examined has been entirely free from all of them. While in cements of good quality the percentages are individually small, they are in the aggregate sufficient to be an element affecting quality that must always be reckoned with when any attempt is made to correlate the results of chemical analysis with physical tests.

As the Newberrys have demonstrated that the lime, soluble silica, alumina and iron are the constituents of a cement that give it value, and further, that whatever the chemical compounds may be that exist in cement the elements are empirically combined in the percentage relations represented by the above formula, Newberry's formula becomes empirically of great technical value, as furnishing a means of comparison by which through chemical analysis the varying qualities of

cements as demonstrated by physical tests, may be explained.

It then becomes of the greatest importance that a method of analysis be followed that would clearly separate the cement, which more or less closely approximates in empirical composition Newberry's formula, from the various substances, noxious and inert, with which it may be associated, that are not cement. It is along this line of investigation that the interests of engineers, and others who control the use of cement, are wholly to be found. It is therefore with surprise that one reads from the progress report of the Special Committee on Uniform Tests of Cement of the American Society of Civil Engineers, that "the determination of the principal constituents of cement—silica, alumina, iron oxide and lime—is not conclusive as an indication of quality. The ash of the fuel used in burning may so greatly modify the composition of the product as largely to destroy the significance of the results of analysis." This surprise vanishes when it is found that Mr. Richardson's scheme of analysis as proposed by the Committee on Uniformity in the Analysis of materials for the Portland Cement Industry of the New York Section of the Society of Chemical Industry (page 225) is recommended.

This scheme begins by finely pulverizing the sample and then pouring upon it 10 c. c. HCl diluted with about 50 c. c. of water. "If anything remains undecomposed it should be separated, fused with a little Na_2CO_3 , dissolved and added to the original solution." This is a method of ultimate analysis. It is no better than Humphrey's method which starts out with fusing the whole sample with Na_2CO_3 . By this method any distinction between the part which is cement and the part which is not cement is impossible. All of the silica, whether sand, ash or soluble silica, is weighed in one mass and called SiO_2 , and means nothing, as only the soluble silica has any value as a constituent of cement. So too, the alumina and iron that belong to the cement that is present, is mingled with the alumina and iron that form a part of all the material that together constitutes the not cement. This committee has given directions for physical tests that are clear, but the suggestions relating to the chemical analysis are vague, inconclusive and practically worthless. The value of a chemical analysis of cement depends absolutely upon how it is conducted, and may

either wholly confirm and explain the physical tests or be wholly worthless for any purpose. Mr. Blount is perfectly correct when he characterizes this scheme as "erroneous."

Nor is Mr. Blount's scheme, which he has used so long, any less "erroneous." He dissolves "the cement (presumably as received) in hydrochloric acid (presumably concentrated), evaporating the solution to dryness, but not intentionally baking the evaporated material, redissolving in hydrochloric acid, filtering, washing, dissolving out the precipitated silica with sodium carbonate solution and collecting the final insoluble residue." He thinks "it may be fairly assumed that a siliceous residue, which has resisted this series of treatments, is inert and valueless as a cementitious material." With this assumption we fully agree, but, why should he assume that material that did not resist this series of treatments is all cement?

It may be that cements burned in briquettes are free from admixture with materials that are not cement, and that will not resist such treatment, but cements burned in rotary kilns contain the ashes of the fuel, which will not resist the action of even cold concentrated hydrochloric acid. My correspondent (page 236) says he cannot add such an excess of lime, as, when combined with the alumina and silica of this ash would make cement, because it will not so combine. The lime remains free and in excess and injures the cement, while the ash remains free and mechanically mingled with the cement both in the clinker and when ground. These ashes are decomposed either by fusion or by strong hydrochloric acid, and the constituents are improperly added to those of the cement.

If an ultimate analysis is desired, by all means use the scheme presented by Mr. Richardson's Committee, a scheme that is well nigh perfect. But excellent as it is, it is not suited to the work in hand, and it is therefore concluded that while the practical value of the labors of Mr. Blount, Dr. Hillebrand and Mr. Richardson's Committee cannot be over-estimated, it is quite clear that the problems presented to a chemist in a cement manufactory, and the problems presented to engineers and the users of cement generally, and the problems presented to Dr. Hillebrand are wholly different and require for their so-

lution consideration of wholly different methods of procedure.

Those engaged in the manufacture of cement can best decide what method of analysis will best solve the problems presented to them. It is evident from the reports above cited that they have decided they require an ultimate analysis. It is not clear to us in what respect the method promulgated by the Committee of the Lehigh Valley section of the American Chemical Society, is superior to the method proposed by Mr. Richardson's Committee, which, as before stated, seems to us as a method of ultimate analysis, well nigh perfect.

So, too, those who use cement and those who control the use of cement can best decide what methods are best suited to the time, place, conditions and identity of the problems presented to them for solution, and it is to these problems that we now address ourselves. We find that the users of cement have not been represented on the committees that have devised these schemes, nor heard in their reports, hence the necessity for giving their problems due consideration.

The Method of Analysis.—As before stated, the cement is used upon the work in progress as it is received from the manufactory. It is subjected to physical tests as it is used upon the work in progress. It should be subjected to chemical analysis as it is used upon the work in progress. It should neither be dried, pulverized nor sifted, because to dry, pulverize or sift it would convert it into a different sample that was not a sample of the cement used upon the work in progress or subjected to physical tests. Moreover, it would be impossible to dry, pulverize or sift the cement that had already been put into cement mortar or concrete, hence a scheme designed to correlate the results of physical tests with the chemical examination of cements, cement mortars and concretes, must, so far as is possible, require that the sample of cement used shall preserve its identity through all of the various tests. It is therefore imperative that the physical and chemical tests shall be made upon the sample just as received and that the mortar and concretes shall be slowly dried at a temperature not to exceed 220° F. in such manner as not to remove any of the combined water. An electrical oven that will maintain a uniform temperature of 220° F. for an indefinite period, is used for this purpose.

Having dried the mortar or concrete at a uniform temperature, the mortar is carefully separated from the stone and each weighed. The proportion of stone to mortar is thus determined. The mortar is then sifted through a No. 10 sieve to remove the gravel. This has to be done in order to secure an accurate weighing of an average sample. Sand used for concrete is seldom, if ever, screened and the mortar therefore contains a certain percentage of gravel that can only be determined accurately in a larger sample than can be used for analysis, hence it must be separated and at the same time weighed and included as a part of the sand.

(1) **Volatile at a Red Heat.**—The first step in the process of analysis is to determine the amount volatile at a red heat. The temperature should be sufficient to expel the carbonic oxide and combined water, but should not be high enough to sinter the assay. Mr. Richardson recommends a blast lamp. We think that a three-tube Bunsen burner is amply sufficient, but a single tube Bunsen is not. An electrical muffle that can be adjusted to a low red heat is superior to anything we have ever used. With two small platinum crucibles, duplicate determinations can be made on 1 gm. of cement each, or 2 gms. of mortar, at precisely the same temperature and with great accuracy. The loss is combined water and carbonic oxide (CO_2) with a small amount of moisture in some cements.

(2) **The Sample.**—Five gms. of the cement or 10 gms. of the mortar are carefully weighed out. Of course, if the cement is reduced to an impalpable powder by supplementary grinding, a fair average may be obtained in 0.5 gm. So too, if all cements that are to be analyzed are first class, a fair average may be had in 0.5 gm.; but, a large part, if not the major part of the cements analyzed are of inferior quality, hence a sufficiently large sample should be weighed out to ensure a fair average mixture of the cement with that which is not cement. In the case of mortars when sand in large amount has been mixed with the cement, the necessity for a large sample is obvious.

(3) **The Solution.**—When analytical work was first undertaken several years ago, I found, in common with others

who attempted to correlate the physical and chemical tests, that no correspondence could be observed.

Believing that Nature could not contradict herself, I was convinced that there must be some defect in the question put to nature, in the chemical analyses; in other words, that the chemical analysis was not properly conducted. This led to the conclusion that the purpose of an analysis was not satisfied when a method of ultimate analysis, in some respects, inadequate, was followed. I therefore sought to arrange a method of analysis that should be proximate. I observed that when concentrated HCl was poured upon a portion of cement in an evaporating dish the reaction was very violent with evolution of heat that was perceptible on the outside of the dish. It was also apparent that much of the combined silica was separated and rendered insoluble, and thus became mingled with the sand and insoluble residue. It appeared that the combined silica should be kept in solution, if possible, and separated by filtration from the insoluble portion. To do this in an effective manner led to a series of experiments in which the attempt was made to first dissolve the lime and other basic elements in combination with CO_2 as carbonates, before decomposing the silicates. A dozen different acids of varying strength were tried all of which decomposed indifferently both carbonates and silicates, and all attempts in this direction were abandoned. A 20 per cent acid (1HCl, sp. gr. 1.2 to 4 H_2O), was then used, which was poured upon 5 gms. of the cement in a casserole, the results being given as No. I in table. The results appearing as No. II were obtained when the cement was carefully and slowly jarred upon the same acid. Another analysis was made by pouring concentrated acid upon the cement, with results given as No. III. Still another was made by pouring upon the cement 10 per cent acid, with still other results given as No. IV. A study of these results led to the suggestion that possibly the active chemism attending the solution in the several instances observed might be responsible for the varying results.

Five gms. were then sifted through a No. 40 sieve upon the surface of 250 c. c. of 10 per cent acid in a No. 8 evaporating dish in such a manner as to reduce the evolution of heat

to the lowest terms and thus keep in solution all of the combined silica that is set free.

The mixture was then vigorously stirred at intervals for half an hour, or until all that would dissolve was in solution, when the solution was filtered and the residue on the filter thoroughly washed with hot water. The results obtained are given as No. V. Assuming that the magnesia, sulphuric oxide and loss at a red heat were correctly estimated in No. I, Nos. IV and V give, respectively, a total of 99.20 per cent and 99.21 per cent. There is a very little difference in the percentages of lime, but the sieve method yields the largest percentage of soluble silica. It was inferred from this result that perhaps a still weaker acid might dissolve more silica, and the attempt was made to decompose the cement with a 5 per cent acid, but without success.

No.	Insoluble in HCl.	Soluble Silica.	Alumina and Ferric Oxide.	Lime.	Magnesia.	Sulphuric Oxide.	Loss at red Heat.	Lime Soluble in H ₂ O.	Alumina Soluble in H ₂ O.
I	20.42	12.24	7.50	55.05	2.19	1.90	1.15	5.27	0.52
II	7.87	16.37	8.88	62.32	2.19	1.90	1.15	5.27	0.52
III	22.39	1.63	8.98	62.74	2.19	1.90	1.15
IV	5.83	17.37	9.00	61.76	2.19	1.90	1.15	5.27	0.52
V	5.79	17.81	8.65	61.72	2.19	1.90	1.15	0.52

The 10 per cent acid used in this work, and hereafter referred to as 10 per cent HCl, is not a solution of HCl containing 10 per cent by weight of dry HCl gas, but is a solution of HCl made by diluting one part concentrated HCl, sp. gr. 1.2, with nine parts distilled water, containing between 4 and 5 per cent of dry HCl and having a sp. gr. of about 1.02. Acid of even this degree of dilution if poured upon dry cement will produce sufficient heat at the point of contact to convert a portion of the silica into an insoluble form. If, however, the directions here given are followed the silica all remains in solution and nothing but the cement is decomposed; 250 c. c. of this 10 per cent acid contains 25 c. c. of concentrated hydrochloric acid, which is equal to about 10 gms. of dry HCl gas, which, in practice, has been found sufficient for the purpose.

In the analysis of cement mortars the cement used is diluted with a large amount of quartz sand. In an examination of any given specimen of cement mortar, the portion of the sand soluble in 10 per cent HCl, while small, should be determined if possible, in a separate sample of the sand used in the mortar, and the result obtained, used in correcting the results obtained from the analysis of the mortar. Ten gms. of the mortar are weighed out and treated as if it were cement, by slowly jarring it on to the surface of 250 c. c. of the 10 per cent acid contained in a No. 8 evaporating dish. The acid should not be heated and the solution should not be hurried as the slow solution of the cement with little or no rise of temperature is essential to the complete solution of the soluble silica and at the same time the complete separation of the cement from the sand and other materials that are not cement.

Concerning this solution of either cements or mortars it is to be remarked, that the sample taken for analysis being identical with the sample selected for physical tests and so treated as not to change its chemical relations to the solvent used, the material treated is separated into the cement which passes into solution and that which is not cement which remains undissolved.

If effervescence follows it indicates the presence of carbonic acid. Traces of H_2S are to be expected. A black residue indicates carbon or soot, which may be estimated by gathering the residue on a balanced filter, weighing, burning off the carbon and again weighing. Neither carbonic acid, carbon nor soot are to be expected in first class Portland cements. More or less CO_2 is usually present in natural cement. Coal appears to be sometimes ground with cement to change its color.

(4) **The Residue.**—Our correspondent furnished us a sample of the coal he was using. Analyzed, it yielded 11.95 and 11.76 per cent of ash, an average of 11.85 per cent which at 380 pounds of cement to the barrel, equaled 4.68 per cent of ash instead of 3 per cent. Of this ash 22.92 per cent was soluble in 10 per cent hydrochloric acid.

The ash consisted of:

Silica	42.94	per cent.
Alumina and ferric oxides.....	41.41	"
Lime (CaO)	9.52	"
Sulphuric oxide SO ₃	3.58	"
Undetermined	2.55	"

100.00 per cent.

The sulphuric oxide was wholly soluble in dilute hydrochloric acid.

Another sample of coal yielded 10.63 per cent of ash, which is equal to 4.2 per cent of ash in the clinker. When analyzed this ash yielded:

Silica	43.30	per cent.
Alumina and ferric oxide.....	38.69	"
Lime	9.12	"

91.11 per cent.

There was undetermined SO₃, CO₂ and a trace of H₂S.

This analysis, as well as the one given above, seems to indicate that the lime in the fuel ash combines to form a soluble compound with a part of the silica, alumina and iron, while the remainder of the silica, alumina and iron, being in excess, still continues in combination in a form not readily decomposed by dilute acids, although easily attacked by concentrated acids.

This explains why some of the very best cements are gelatinized with only a little more than a trace of matter undecomposed by concentrated acids and yield a residue to dilute acid having the appearance of ashes, but containing no lime, and less in amount than the ash contained in the coal used, as is shown in the analytical results given above.

When an attempt is made to make a chemical examination of cement mortars and concretes the impossibility of using an ultimate method is at once obvious. The average specimen of quartz sand is nearly or quite inert to the action of 10 per cent HCl. Acid of this strength therefore will dissolve the cement and leave the inert sand when a sample of cement mortar is under examination. With this acid the character of the cement becomes at once apparent. If carbon

or carbonic acid are present, they are at once set free. If unburned cement rock has been ground with the cement, the excessive amount of fine insoluble material in the sand is at once discovered. With a first class Portland cement and clean sand, the residue from the solvent is found to be almost wholly clean sand.

The cement in the cement mortar or concrete must be the same as that which was used in the work in progress, from which the sample of mortar or concrete was taken. It must be the same as that subjected to physical tests. It can neither be dried, pulverized nor sifted to remove clinker and other foreign matter. It must be taken with all of its properties, good and bad. It is imperative that it should be analyzed by precisely the same method that is followed in the analysis of the cement.

A portion of the cement, as it is brought in from the work in progress is subjected to physical tests. Another portion of the cement just as it is brought in, is subjected to chemical analysis. Frequently the broken mortar briquettes are subjected to analysis. Frequently also, portions of cement concrete are brought in from the works. These are broken up, the mortar separated from the stone and both dried at a temperature not to exceed 220° F. and weighed. As the mortar consists of about 70 per cent sand, 10 gms. are weighed out in pieces, free from dust, and large enough to secure an average, which at the same time shall be free from pebbles of gravel. Either 5 gms. of this cement or 10 gms. of the mortar are placed in 250 c. c. of 10 per cent hydrochloric acid, and, after standing several hours, or over night, the insoluble residue is separated by filtration, dried, ignited and weighed.

If an analysis of this residue is desired, it is fused with Na_2CO_3 , the melt dissolved in 10 per cent HCl and water, the silica separated and the solution proceeded with separately, according to the following scheme.

(5) **Silica.**—If extreme accuracy is desired, the method described by Dr. Hillebrand beginning with (3) Separations, (p. 222) is recommended; or, if it is preferred, the scheme of Mr. Richardson (page 225), beginning at the "filtrate is again evaporated to dryness" under "Silica," may be employed.

For ordinary technical analysis the double evaporation of the solution from 5 gms. is not necessary.

The filtrate from the solution in 10 per cent HCl, with the washings are evaporated in a No. 8 evaporating dish over a water bath. A large dish is selected in order that the residue from evaporation may be spread out in a thin layer over a large surface. The silica solution is evaporated over night over a water-bath heated by an electrical stove. Morning usually finds the residue dry at a temperature below the boiling point of water. Heating to a temperature of about 250° F., on an electrical stove completes the dehydration at a uniform and low temperature.

The dried residue, distributed in a thin layer upon the bottom of the evaporating dish, is drenched with concentrated HCl, care being taken that every particle of the residue be wetted with the acid. The iron will all pass into solution if the baking has been conducted with care and is not excessive. The excess of HCl is evaporated, the residue wetted with concentrated HCl and about 300 c. c. of distilled water added. The solution is then boiled, filtered hot and the precipitated silica thoroughly washed with boiling distilled water. I am not prepared to say that small quantities of silica do not remain in solution on a single evaporation, but for technical purposes it is a negligible proportion of that contained in 5 gms., when evaporated and dried as here directed. The silica is then ignited and weighed without blasting, the errors being practically "compensating errors."

(6) **Alumina and Ferric Oxide.**—The filtrate from the silica with the washings is poured into a graduated liter flask and the solution made up to one liter. After thorough agitation, two portions of 100 c. c. each, are placed in two beakers, ammonium hydroxide added in slight excess and about 150 c. c. of distilled water. The excess of ammonia is boiled off and the precipitated alumina and ferric oxide is gathered on a filter. The receptacle for the filtrate is removed, the filter filled with 10 per cent HCl and as it passes through the filter is received into the first beaker and any precipitate adhering to the sides is dissolved off. By proceeding in this manner the whole of the alumina and iron is again brought into solu-

tion; ammonia is again added and the precipitate is again brought upon the filter, the filtrate being added to that first obtained. As the amount of cement contained in the original 100 c. c. of solution is only 0.5 gm., the alumina and ferric oxide is rarely sufficient in amount to admit of its being removed from the filter. After being thoroughly washed in boiling water it is dried and burned at a low red heat and weighed. If this procedure is followed with reasonable care the amount of iron reduced from the peroxide will be insignificant.

(7) **Lime.**—The united filtrates from the alumina and iron is then heated to boiling and a slight excess of a saturated solution of ammonium oxalate is added and the boiling continued until the precipitate becomes granular. It is well to set the beaker away over night. It should stand at rest at least two hours, when the precipitate is collected on a filter and washed with very dilute ammonium hydroxide. The dried precipitate is ignited, the paper burned off over a Bunsen lamp, when the crucible is placed over a blast and blasted 15 minutes. The CaO is then cooled and weighed.

(8) **Magnesia.**—The filtrate from the CaO is rendered acid with HCl and evaporated on the steam bath to about 150 c. c., 30 c. c. of a saturated solution of $\text{Na}(\text{NH}_4)\text{HPO}_4$ are added and the solution boiled for a few minutes, and cooled by placing the beaker in cold water. After cooling, NH_4OH is added cautiously with constant stirring, avoiding more than a slight excess until the crystalline precipitate begins to form. The stirring is then continued for several minutes, after which it is set aside for several hours or all night in a cool place, after which it is filtered. If, as will be found in the majority of instances, the precipitate is a trace or but little more than a trace, the filter containing the precipitate is burned off and thoroughly blasted, cooled and weighed. If the precipitate is of considerable amount, it is redissolved in hot dilute HCl, the solution made up to about 100 c. c., 2 c. c. of a saturated solution of $\text{Na}(\text{NH}_4)\text{HPO}_4$ and NH_4OH , added separately, drop by drop, with constant stirring until the precipitate is again formed. It is then allowed to stand at least two hours in a cool place, filtered, blasted, cooled and weighed as MgP_2O_7 .

For technical purposes the lime and magnesia are easily determined with one precipitation each, although each may be contaminated with a trace of the other.

(9) **Sulphuric Oxide.**—For sulphuric oxide, two portions of 100 c. c. each are taken from the solution left in the liter flask from which the silica has been removed. These portions in a beaker glass are heated to boiling and 10 c. c. of a saturated solution of BaCl_2 are added, drop by drop, from a pipette, and the boiling continued until the precipitate has formed, when it is set aside over night. It is then filtered, ignited and weighed.

If a determination of total sulphur is required the method followed by Mr. Richardson's Committee is recommended. (Page 228.)

(10) **Alkalies.**—It is rare that for technical purposes a determination of carbon dioxide or alkalies is necessary. The recommendation of Mr. Richardson's Committee that "the well known method of Prof. J. Lawrence Smith is to be followed, either with or without the addition of CaCO_3 with the NH_4Cl , cannot be improved.

(11) **Carbon Dioxide.**—If a determination of CO_2 is desired any one of the many approved methods and apparatus devised for that purpose is recommended.

While we are aware that sometimes for special reasons, a very elaborate and accurate analytical examination of a sample of cement is desirable, such an examination is seldom or never required for cement mortars. For the purposes under discussion the following named determinations have been repeatedly demonstrated as furnishing all of the data necessary for a correlative examination of cements, cement mortars and concretes:

- (1) Matter volatile at a red heat.
- (2) Matter insoluble in 10 per cent HCl .
- (3) Soluble silica.
- (4) Alumina and ferric oxide.
- (5) Lime.
- (6) Magnesia.
- (7) Sulphuric oxide.

It is not necessary that analytical methods furnishing results accurate to a thousandth of a per cent, should be followed, because it is not possible to use samples that agree with each other to any such degree of parallelism. This statement should not, however, be understood as being regardless of accuracy, which is at all times to be held as the cornerstone of effective analytical work. Yet, while accuracy is never to be lost sight of, the time required to obtain results of practical value is a very potent factor in all technical operations and it is constantly forcing a compromise between accuracy regardless of time and speedy results obtained regardless of accuracy. In the interest of such a compromise we have recommended the scheme as above stated.

In order to further test the value of this scheme as furnishing results correlative with physical tests, four samples of cement were selected and numbered.

No. 770a was a strictly first class American Portland cement.

No. 771a was a so-called "improved" cement alleged to have been made by mixing 770a with a natural cement.

No. 774a was another good American Portland cement.

No. 775a was another "improved" cement made by mixing 774a with a natural cement.

These four cements were made into mortars with standard quartz in the proportion of one part of cement and three parts of quartz by weight.

The cements were made into briquettes neat and the mortars were also made into briquettes. All of these briquettes were broken in two series, one of seven days and the other of twenty-eight days. The cements and broken briquettes were analyzed according to the scheme above set forth.

The silica was determined with and without blasting and with a second evaporation. The amount of silica obtained from the second evaporation varied from 0.11 to 0.55 per cent. The amount depends entirely upon the care that is exercised in the first evaporation. With complete burning over a three tube Bunsen lamp the reduction of weight by blasting was

0.1 per cent, and with careful manipulation the amount obtained by a second evaporation was 0.11 per cent. These sources of error compensate each other and while they are errors, they are of no account in a technical analysis. No reckoning can be made with careless manipulation. Careless manipulation was purposely indulged for the purpose of observing its effects. These effects are fully exhibited in the table given below.

The great value of chemical analysis when properly conducted for the explanation of physical tests, when applied both to cements and mortars and the complete correlation of such analyses with such tests are clearly and emphatically set forth in the results exhibited in the table.

CHEMICAL ANALYSES.

NEAT CEMENTS.

Laboratory Number.	770a.	774a.	771a.	775a.	Average of seven Samples of American Portland Cement.
Volatile at a red heat, per cent	0.65	2.80	6.55	7.72	1.79
Insoluble in 10 per cent HCl....	3.63	5.68	8.16	10.31	4.38
Effervescence observed	none	none	none	none	none
Carbon observed	none	trace	1.93	coal	none
Soluble silica, 1st evaporation, per cent	17.45	18.39	17.09	18.35
Loss by blasting, per cent.....	0.10
2d evaporation	0.30	.039	0.11	.055
Soluble silica corrected, per cent	17.75	18.78	17.20	18.30	18.45
Alumina and ferric oxide, per cent	8.46	9.34	8.66	10.21	9.46
Lime, per cent	62.34	59.73	53.56	48.06	61.89
Magnesia, per cent.....	2.25	2.07	1.96	trace	1.78
Sulphuric oxide, per cent.....	1.41	1.63	trace	1.70	1.87
Undetermined, per cent	3.51	none	1.98	2.70

PHYSICAL TESTS.

NEAT CEMENTS.

7 days, lbs. per square inch....	770	750	275	233
28 days, lbs. per square inch....	826	828	288	277

CHEMICAL ANALYSES.

MORTAR, 1 TO 3 BY WEIGHT.

Laboratory Number.	Theoretical Composition of Portland Cement Mortar 1 to 3 by weight.				
	770c.	774c.	771c.	775c.	weight.
Volatile at a red heat, per cent..	4.93	4.64	4.17	4.80	4.50
Insoluble in 10 per cent HCl, per cent	71.27	75.38	77.47	78.20	72.70
Effervescence observed	slight	slight	active	active
Carbon observed
Soluble silica, 1st evaporation, per cent	4.21	3.30	4.04
Loss by blasting, per cent.....	0.009	0.094	0.091
2d evaporation, per cent....	0.01	0.041	0.066
Soluble silica corrected, per cent	4.21	3.25	2.32	4.02	4.20
Alumina and ferric oxide, per cent	2.24	1.74	2.39	2.04	2.16
Lime, per cent	15.79	13.83	12.53	10.85	14.12
Magnesia, per cent	trace	trace	trace	trace
Sulphuric oxide, per cent.....	trace	trace	trace	trace
Undetermined, per cent.....	1.55	1.18	1.12	0.10	2.32

PHYSICAL TESTS.

MORTAR, 1 TO 3 BY WEIGHT

7 days, lbs. per square inch....	231	187	79	64
28 days, lbs. per square inch....	286	235	140	132

In the examination of concretes from public works a different basis is used since the New York City specifications require that parts shall be taken by measure, while analyses are expressed in parts by weight, it was therefore necessary to determine the equivalent by measure, in percentage by weight. A number of experiments were made upon which to base this estimate. The unit measure of the said specifications is a cement barrel and the mortar is to be made by adding to it three equal barrels of sand. A barrel of Portland cement weighs 380 lbs. net. Obviously, to get the weight of three barrels of sand, the capacity of a cement barrel must be known. This, however, is a variable quantity, owing to the fact that cements of different brands vary in specific gravity, and consequently in bulk for a given weight. Thus the capacity of Portland cement barrels range from 3.2

cu. ft. to 3.8 cu. ft. The average of the barrels of some twelve brands of well-recognized first-class Portland cements shows a capacity of 3.34 cu. ft.

Seven samples of sand from dealers in this city who supply contractors, were dried and carefully weighed, showing a range from 90 to 101 lbs. per cu. ft., the average being 97.1 lbs. per cu. ft.

Broken stone of the size commonly known as 1½ ins., containing 48 to 50 per cent voids, was found to weigh, when dry, approximately 92 lbs. per cu. ft.

After a number of concretes had been analyzed air dry, it was found that the percentage of water in the air dried concrete must be determined at a constant temperature. It was also desirable that the whole sample should be dried at a constant temperature, in order that the proportions of stone and mortar might be comparable. An electrical oven was procured in which 2 to 3 kilograms of concrete could be dried at a constant temperature of 220° F. The specimens still contained an average of combined water amounting to 4.5 per cent of the mortar, or about 64 lbs. of water to one barrel of cement.

Therefore the following table shows the composition of a good average Portland cement concrete in the proportions of 1-3-6 to be as follows:

	Cement.	Sand.	Broken Stone.	Water.
Volumes	1.	3.	6.
Cubic feet	3.33	10.02	20.04
Pounds	380.	973.	1844.	64.
Per cent	11.65	29.84	56.55	1.96

Aside from the fact that these percentages are deduced from general averages, and may, therefore, show a variation from particular or individual instances, they are also subject to a certain modification for the following reason:

When an analysis of the concrete is attempted, the first step after drying the mass at 220° F. is to effect a complete mechanical separation of the broken stone and mortar. By using a sieve of ten meshes to the linear inch, this separation can readily be made, the only source of error lying in the

amount of gravel that is contained in the sand, and which in practice, is never screened. This error would increase the percentage of stone and diminish the sand in the mortar by a small and uncertain amount. Determined by this method, the average percentage of stone and gravel in a concrete of good quality should amount to about 60 per cent, as against 56.55 per cent in the above table.

This figure will vary with the different cements possibly 2 per cent with the same kind of stone. As the specific gravity of cements varies, and as also the specific gravity of the sand and stone to a less extent, the relative weights of a unit volume, or multiples thereof, will vary to a certain extent. It was found, however, that in those cases where the per cent of the stone is highest and the cement lowest, that the cement is light from excess of unburned cement rock, which is evidently added intentionally for purposes of adulteration. The percentage of stone in the concretes ranges from 77 per cent to 52 per cent. These figures exhibit a range of 25 per cent. So wide a difference is only to be accounted for on the ground of gross carelessness in mixing the concrete.

In order to establish a standard of comparison for the proper proportions by weight between the average first-class Portland cement and sand in a cement mortar, as shown by a chemical analysis, an estimate was made based on the analyses made of seven first-class American Portland cements, and also a determination of the soluble portion of the sand in general use in the preparation of concrete mortars. The per cent of mortar found insoluble in 10 per cent HCl was 4.38 per cent. The average amount of sand soluble in 10 per cent HCl, was found to be 1.07 per cent. From these figures, and on the basis that the mortar contains.

1 vol. dry cement, 3.34 cubic feet.....	380 pounds.
3 vols. dry sand, 10.02 cubic feet.....	973 "
Water in combination, 4.5 per cent.....	64 "

Total weight of mortar.....1,417 pounds.

the percentages of matter, soluble and insoluble, in the mortar are readily deduced as follows:

	Soluble.	Insoluble.
Cement, 380 pounds.....	(95.62%) 363.35 lbs.	(4.38%) 16.65 lbs.
Sand, 973 pounds.....	(1.07%) 10.41 lbs.	(98.93%) 962.59 lbs.
Total	373.76 lbs.	979.24 lbs.
Per cent of mortar.....	26.37 per cent.	69.13 per cent.

The composition of average cement mortar as thus found is:

Insoluble in 10 per cent. HCl.....	69.13 per cent.
Soluble in 10 per cent. HCl.....	26.37 "
Volatile at red heat.....	4.50 "

Total	100.00 per cent.
-------------	------------------

Of the 26.37 per cent of the mortar that is soluble in 10 per cent HCl there are certain constituents which go to form the active principle or cementing power of the mortar or concrete. These, of course, are principally contained in the cement and consist of soluble silica, alumina and iron oxide and lime.

The proportions of these ingredients in terms of percentages of the mortar were determined as follows, by using data obtained from previous work in this line, thus:

An average of the analyses of the seven first-class Portland cements previously referred to showed the proportions of the above mentioned ingredients to be, in terms of percentages of the cement:

Soluble silica.....	18.45 per cent.
Alumina and ferric oxide.....	9.46 "
Lime	61.89 "

Analysis of the sand for the same purpose gave in terms of percentages of the sand:

Soluble silica.....	0.25 per cent.
Alumina and ferric oxide.....	0.23 "
Lime06 "

In both the cement and the sand there are, of course, other ingredients either insoluble or inactive which need not be considered in this connection.

Then if we consider, as before, that a Portland cement mortar (1 to 3 by volume) will contain 380 lbs. of cement, 973 lbs. of sand and 64 lbs. of water in combination, the quantities of the soluble silica, alumina and ferric oxide and lime in the mortar will be as follows:

	Soluble Silica.	Lbs.	Al. and Fe. Oxides.	Lbs.	Lime.	Lbs.
Cement (8.45% of 380)	70.11	(9.46% of 380)	35.95	(61.89% of 380)	235.18	
Sand (10.25 % 973)	2.43	(0.23% of 973)	2.24	(.06% of 973)	0.58	
Total	72.54		38.19		235.76	

Which in percentages of mortar amount to:

Soluble silica.....	5.12 per cent.
Alumina and ferric oxide.....	2.70 "
Lime	16.64 "

Making a total of..... 24.46 per cent.

which subtracted from 26.37 per cent (the entire amount soluble in 10 per cent HCl as shown in the schedule on page 259), leaves 1.91 per cent of the soluble matter which is inactive, consisting of magnesia, sulphuric oxide, alkalies, etc.

A summary of the results obtained from the preceding calculations then shows that a good average Portland cement concrete, in the proportions of 1-3-6 by volume, should give in percentages by weight approximately:

Concrete	{	Broken stone. 52.55% to 60%		{	Insoluble, 68.15%		{				
		Mortar consisting of cement, sand and water in combination 40% to 43.45%	{		Volatile at red heat, 4.50%						
					Soluble, 26.37%						
					{						
					Inactive, 1.91%						
					Active, 24.46%			{			
					Soluble silica . 5.12%		{				
					Alumina and ferric oxide. 2.70%						
					Lime 16.64%						

In order to ascertain to what extent these figures, shown on page 259, are confirmed by the practical work of the laboratory, briquettes were made of a first-class Portland cement, with standard crushed quartz, proportions 1 to 3 by volume, and also with a quartz sand in very general use in concrete constructions about the city of New York. The cement was first analyzed when the briquettes were analyzed, the first contained 68.19 per cent insoluble in 10 per cent HCl, the second 68.07 per cent, and the third 69.55 per cent. A fourth briquette was made from mortar taken from a mortar board where cement concrete was being mixed by hand. This mortar, when air-dried, contained 71.3 per cent of matter insoluble in 10 per cent HCl. Another briquette, from a mortar made from another cement contained 72.14 per cent insoluble in 10

per cent HCl. The average insoluble matter in these five mortars was 69.85 per cent. It is probable that with different sands and cements, and for practical purposes, an average of 70 per cent would not be far from correct. The average amount of active cement found in these five cement mortars by Newberry's formula is 23.17 per cent. As an empirical formula, it has been found to indicate in instances, now amounting to hundreds, the value of a cement for practical purposes, in a most satisfactory manner.

In order to determine the percentages by weight of soluble silica, alumina and iron oxide taken together, and lime, the sum of which percentages indicates the entire amount of active cement in any cement mortar or concrete, according to Newberry's formula, it was assumed that no injustice would be done in any comparison that might be made if the soluble silica was used as a unit of comparison after the following manner: The sand used was a clean quartz containing about 1 per cent of iron oxide and other matter, which was soluble in 10 per cent HCl. The amount so soluble was sufficient to increase the percentages of alumina and iron oxide present, but the amount of sand used in the mortar being very variable, the amount of iron accruing from this cause was inconstant. It was therefore determined to assume on the basis of the average results that the amount of alumina and iron oxide legitimately constituting the active cement present shall be computed at one-half the soluble silica present. Then, using Newberry's formula, and multiplying the percentage of soluble silica by 2.8, and one-half of that percentage by 1.1, and adding the products together, the sum thus found represents the percentage of lime that, in combination with soluble silica, alumina and iron oxide, formed the active cement present. The soluble silica found by analysis, plus one-half such amount computed as alumina and iron oxide, plus the lime computed as above indicated, equals the percentage of active cement found in any concrete.*

*Report of the Commissioners of Accounts of the City of New York, July 27, 1905.



PART III.

THE PHYSICAL PROPERTIES OF SOLID BITUMENS.

CHAPTER XV.

SPECIFIC GRAVITY, ETC.

The specific gravity of solid bitumens may be taken by any known method. As natural bitumens are seldom pure, and the mixtures vary even in the same kind of bitumen, from the same deposit, any comparisons based on specific gravity give little satisfaction and are of little value.

There are experimenters who claim to have obtained satisfactory results when operating upon bitumens that have been obtained by the evaporation of solutions of natural bitumens obtained by various solvents, thus excluding the impurities. These results vary very little from 1,000. Some of these extracts sink while others float. The differences are so small as to signify very little. The Westphal balance is a convenient instrument, where extreme accuracy is not desired; but close work must be done with the bottle or the balance alone. In the experience of the author, but little is learned to compensate for the time required in the determination of the specific gravities of solid bitumens.

SOFTENING POINT.

As a means of comparison the determination of the softening point is of some value. It consists in the empirical determination of the temperature at which a given specimen of bitumen will melt or lose form. A variety of methods have been contrived for making this determination, which, taken together as a group, passes into another group that is designed to ascertain the temperature at which a given specimen will flow. The dividing line between the two groups is arbitrary and not very distinct. I shall describe the apparatus as referred to one class or the other by their inventors.

MABERY AND SIEPLEIN.

C. F. Mabery and O. J. Sieplein investigated the softening and melting points of solid bitumens and suggested the

following described apparatus (Fig. 16). "In a glycerine-bath in a beaker of moderate size is placed a narrow beaker closed with a cork through which is passed a thermometer. There is also inserted through the cork close to the side of the narrow beaker, a strip of metal, $\frac{1}{2}$ in. wide, bent over the side of the beaker as a support, and extending to within $\frac{1}{2}$ in. of the bottom of the beaker. The lower end of the metal strip is bent at a right angle and the narrow corners are bent upwards. The bend in the metal is used as a support for the section of asphalt which is pressed on the points, formed by the corners of the metal. The dimensions of the apparatus used by us

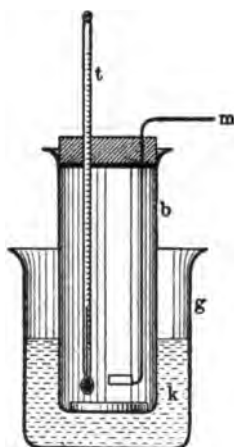


Fig. 16.—Mabery and Steplein's Apparatus.

are given, but evidently the only constants need be the distance of the thermometer from the specimen; the distance of the metal from the bottom of the beaker, the width of the metal strip and the dimensions of the specimens to be tested. With the metal strip $\frac{1}{2}$ in. wide the specimen to be tested is cut or molded of sufficient length to project $\frac{1}{4}$ in. on either side of the metal. The observation consists in noting the temperature at which the specimen softens and becomes sufficiently fluid to fall on either side of the metal support and just touch the bottom of the beaker. We found it convenient to place a disk of copper on the bottom of the inside beaker, since it could be removed after the observation, and the as-

phalt that had fallen more conveniently cleaned than from the bottom of the beaker. While a Bunsen flame is the more convenient source of heat, an alcohol or oil lamp can be used. Evidently the time of heating should not vary widely, although we have found a variation of five minutes had no appreciable effect on the melting points.

"The dimensions of the different parts of the apparatus are:

	Inches.
Width of outside beaker.....	2½
Height of outside beaker.....	3½
Width of inside beaker.....	1½
Height of inside beaker.....	4½
Width of metal support.....	½
Length of lower bend of support.....	¾
Distance of specimen from false bottom of beaker..	½
Standard size of specimen.....	1 x ½ x ¼

"In testing the efficiency of this method, observations were made of the initial temperature, of the temperature at the time when the softened material just touched the bottom of the beaker, and the time (duration) of heating."*

For high melting points, an air-bath or a paraffine-bath is used.

J. KOVÁCS.

"For the determination of hard and soft grade asphalts the apparatus is described as follows:

"On a sand-bath S (Fig. 17), 160 mm. (6 in.) diameter, with a 10-mm. (3/8 in.) layer of sand, a beaker, O, is placed, of about 110 mm. diameter (4 1/3 in.) diameter and 160 mm. (6 in.) high, containing sufficient rape-seed oil or glycerine to cover the beaker—L, 90 mm. (3½ in.) diameter and 160 mm. (6 in.) high—three-quarters of its height. In this air-bath the dropping frame is placed, Fig. 18, top view; Fig. 19, side view. It consists of a strong brass disc, 3 mm. (1/8 in.) thick and 83 mm. (3¼ in.) diameter, perforated in the center for a thermometer and with four perforations of 2 mm. (3/32 in.) diameter, around each of which a brass cylinder of 12 mm. (½ in.) inner diameter and 15 mm. (5/8 in.) high is

**Jour. Am. Chem. Soc.*, xxiii, p. 16; *Jour. Soc. Chem. Ind.*, xx, p. 394; Köhler, p. 352.

soldered. The disc is supported on three feet, each 60 mm. ($2\frac{3}{8}$ in.) high. A regulated Bunsen burner is placed under the sand-bath, so that the temperature of the air-bath is evenly raised in each determination. The air-bath is supported from the ring of a retort stand, and the annular space between it and the sides of the oil-bath is covered by a large, flat, perforated cork. The tubes of the dropping frame should be numbered 1-4.

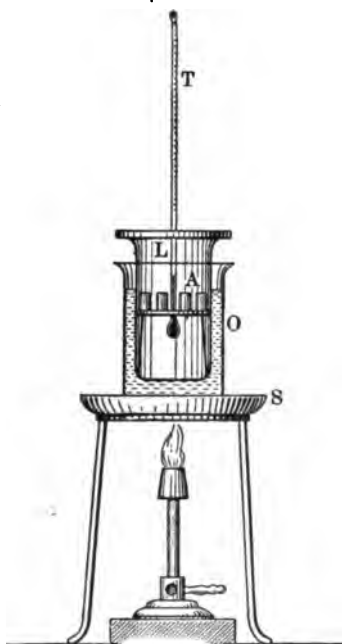


Fig. 17.

J. Kovacs' Apparatus.

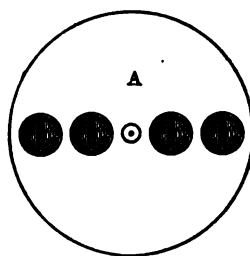


Fig. 18.



Fig. 19.

"In testing hard asphalt, a portion is formed into a pellet, weighed, and allowed to stand from 10 to 20 minutes. A pellet is then inserted in each of the numbered tubes of the dropping frame, which is immediately placed in the air-bath with a thermometer; a thermometer is also suspended in the oil-bath, and a gas burner is placed under the sand-bath. After some time the softened bitumen is visible underneath the perforated disc, and the instant it drops, the temperature of the air-bath is noted. Bitumens for foot pavements should not drop inside 80°C. , and for roadways, not under 105°C.

"It is impossible to give a process for precisely determining the adulteration of a natural bitumen with petroleum pitch up to 20-25 per cent., but its presence can be proved quite well by the chemical tests described on pages 198-202."*

The following are some results that were obtained with this apparatus:

Kind of Asphalt.		Dripping Temperature.
No. 1.	Dalmatian asphalt.....	97.0° C.
No. 2.	Trinidad asphalt	93.5° C.
No. 3.	Tartaros asphalt	114.0° C.
No. 4.	Normal	105.0° C.
Kind of Pitch.		Softening Point.
Soft.		40° C.
Medium.		60° C.
Hard.		80° C.
		Melting Point.
		50° C.
		70° C.
		90° to 110° C.

According to Lunge (Lunge-Kohler, *Ind. d. Stein Kohlenters u. Ammoniaks* 4 Ed. 1, p. 431), chewing is a practical test. If it chews easily it is soft, if with more difficulty, it is medium; if it becomes pulverized in chewing, it is hard. The soft pitch is glistening and blacker than the hardest, which contains more matter which is of a grayish tint.†

HOLMES.

J. G. Holmes remarks as follows concerning researches upon pitch. Several pieces of pitch from different parts of the sample are cut into cubes of about 13 mm., then they are stuck upon wires which are heated and the pitch fastened upon them. The pieces are then sunk in a vessel holding 500 cc. of water and the temperature simultaneously raised at the rate of about 5° a minute. The thermometer should be inserted in the vessel in such manner that it should be 4 or 5 cm. from the bottom, and the cubes should be immersed even with the thermometer bulb. As soon as the temperature rises the cubes are taken out from time to time and squeezed together with the fingers. The temperature is noticed at which the following appearances are shown:

1. Softening.
2. Strong softening.
3. Melting.

*Chem. Rev. d. Fett u. Harz Ind. 1902, p. 156. Jour. Soc. Chem. Ind. xxi, p. 1077, 1902.

†Köhler, Chem. u. Tech. d. Nat. u. Kunst. Asphalte, p. 353.

Softening is indicated when the pitch can be drawn out spirally with ease; strong softening when it yields easily to the fingers; and melting when the pitch drops off the wires.*

THE FRENCH METHOD WITH CYLINDERS.

Accurate results are obtained in the following way, which is used in the French industry. The tin cylinder (Fig. 20), contains a horizontal partition into which are soldered five tubes, closed at the bottom. The middle tube serves for the introduction of a thermometer, the four others for the reception of ground and sifted pitch. The large pieces and the dust should be removed by means of a sieve. The pitch powder is loaded with an iron piston and rod of a determined weight, which rods, as well as the thermometer, pass through holes in the cover of the cylinder, which serve as guides. The cylinder is filled with water, or, for pitches of high melting point, with solution of common salt, to a point above the top of the tubes, and heated with a lamp until the pistons sink in the melted pitch, which temperature should be noted as the melting point.

A massive steel cylinder is better than this tin vessel in which are bored five openings for the tubes and the thermometer.†

MUCK.

Pitch Stick Method.—According to Muck, the determination of the softening temperature is accomplished in the following manner: From the sample of pitch to be examined, small cylindrical sticks of 4 mm. diameter and 100 mm. length are molded; about 20 mm. of the stick is bent around the bulb of a thermometer and held by a rubber band in such a manner that the stick stands parallel with the thermometer tube. Thus mounted the stick and tube are placed in a Becker glass filled with water, to which is attached a vertical stirrer, and heated until the long leg of the stick of pitch begins to bend over. This method is as much to be depended on as are the others of similar purpose already proposed.‡

*Lunge-Köhler, *Ind. d. Stein Kohlenteers u. Ammoniaks* 4, Ed. 1, p. 432. Köhler, p. 354.

†Köhler, *Chem. u. Tech.* s. 355.

‡*Zeitschr. f. Berge, Hutten- u. Salinenwesen*, 1885, vol. 37; Köhler, s. 355.

BUCHANAN.

Another Pitch Stick Method.—Buchanan sticks a suitable pitch stick to a thermometer tube placed in a dry test tube and heated in a water-bath. The pitch first softens and then falls off, which indicates the melting point. In this way he found the melting point of hard pitch to be at 80° , of medium at 55° , and of soft pitch at 50° .*

SCHENK ZU SCHWEINSBERG.

Method with Bent Tubes.—E. Schenk zu Schweinsberg uses the following method for determining the melting point of pitch and the condition of fluidity or flowing. A glass tube

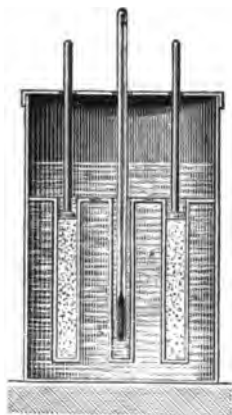


Fig. 20.
French method with cylinders.

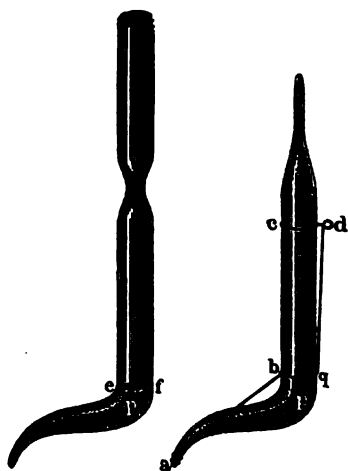


Fig. 21.
Schenk zu Schweinsberg's method.

(Fig. 21) about 7 mm. wide and 25 mm. long, is bent and drawn out over a gas flame into the form shown in Fig. 21. The lower part is then filled to the line *ef* with pitch finely crushed in a mortar; in case the pitch is too soft for the mortar, small balls are formed and the lower bent part of the glass tube filled with them. Upon the surface of the pitch is placed a drop of mercury. The tube is next drawn out at its narrow part in the flame to a pointed capillary tube. A platinum wire is then fitted to the tube *abcdq*, by which a small sling is formed for the support of the point of the glass tube,

**Jour. Soc. Chem. Ind.*, 1894, p. 1098. *Köhler*, p. 356.

while the wire at *bq* and *cd* makes a ring around the tube in which it is slung; at *d* a small loop is made in this wire into which is inserted a small glass rod which serves as a support for the apparatus in a Becker glass of water. Beside the small tube a thermometer is suspended, the bulb of which shall be at the same level as the specimen of pitch. The water is very slowly warmed and any gas bubbles that adhere to the surface of the apparatus may be removed by the tip of a feather. The pitch settles together with the rise of temperature, so that finally the mass of the pitch is only one-half the original volume. As the melting point of the pitch is reached it has the appearance of expanding. The approach of the melting can be most easily observed at the bent portion and the point of the apparatus. As soon as the expansion commences, the thermometer is read, which now gives the melting point of the pitch. The warming is continued slowly until the pitch in the tube rises, when the drop of mercury sinks and is enclosed by the fluid mass. This fluidity of the pitch, whereby the whole lower part of the tube is filled with fluid pitch and mercury, Schenck zu Schweinsberg calls the practical melting point and reads the temperature corresponding to these phenomena. He demonstrates as soft pitch all whose melting point is under 60° , as medium hard all whose melting point is from 60° to 99° , and as hard those whose melting point lies above 100° .*

KLIMONT.

Test-Tube and Cone Methods.—J. Klimont declares the method of Schenck zu Schweinsberg to be the most reliable for the determination of the softening and melting temperatures of coal-tar pitch, but it should be pointed out that only in the hands of an analyst who has made them frequently, will it give results to be depended upon, as the expansion as well as the sinking of the drop of mercury in the fine pitch dust, which at the same time covers the surface of the same, is very difficult of recognition by an untrained eye in no way accustomed to observe. Klimont fixes both as the important points in technical research by means of the following simple tests:

*Osterr. Zeltschr. f. Berg- u. Huttenwesen, 1890, p. 463; Zeltschr. f. angew. Chemie., 1890, p. 704; Köhler, p. 356.

(1) An ordinary test-tube is filled with the finely pulverized pitch by pouring it through a funnel with a long neck, the bottom of the tube is jarred gently upon the table until the powder is collected into a compact mass which a little more than fills the curved part of the test-tube. Then if the pitch is soft or medium hard, the test-tube is suspended by a wire in a Becker glass of water with a thermometer the bulb of which shall be at the same level as the pitch. For hard pitch the determination is made in a glycerin-bath. It is slowly warmed over a Bunsen burner, the flame of which is 2 cm. in height; as soon as the edge of the pitch dust or the little balls melt together and the mat of pitch dust will brighten the sides of the vessel, the melting process begins and the temperature is read. As soon as the pitch on the sides melts, then, finally, the whole surface will become smooth and glisten. As soon as this moment is observed, which indicates the end of the melting process and also Schenk zu Schweinsberg's point of fluidity, the temperature is noted.

Still more noticeable are the temperatures by the following tests:

(2). The pitch under examination is quickly softened in a flame until it will knead; it is then rolled and drawn into a cone about 3 mm. base and 5 mm. high. The point is now seized with the pincers, the base softened in a flame and the cone stuck to the bottom of a small tube 7 mm. in diameter by 35 mm. high, so that the whole cone stands perpendicularly. The tube is reversed until the cone is cold. Mercury is then poured into the tube until the point of the cone is no longer in sight and the tube is warmed in a Becker glass of either water or glycerine, as before described.

At the surface of the mercury a black point suddenly appears. The temperature at which this phenomenon occurs is the beginning of the melt and corresponds with the melting point of Schenk zu Schweinsberg. By warming longer the pitch drop spreads out upon the mercury and this temperature approaches the point of fluidity of Schenk zu Schweinsberg.

By a comparison of the method of Schenk zu Schweinsberg with that of Klimont, medium hard pitch gave the following degrees of temperature:*

**Zeitschr. f. angew. chem.*, 1900, p. 761; Köhler, p. 357.

	Schenk zu Schweinsberg.		Klimont (1).		Klimont (2).	
	Melting Point.	Point of Fluidity.	Melting Point.	Point of Fluidity.	Melting Point.	Point of Fluidity.
	Degs.	Degs.	Degs.	Degs.	Degs.	Degs.
No. 1	62	66	64	67	64	67
No. 2	60	65	60	65	60	63
No. 3	80	85	79	80	79	84
No. 4	52	57	52	57	52	57
No. 5	60	65	60	66	60	63

KRÄMER AND SARNOW.

Straight Tube Method.—According to G. Krämer and E. Sarnow most of these methods for the determination of the melting and softening points of asphalts and asphaltic bodies are uncertain, because they are so dependent upon the personal equation that differences of 5 to 10° are not of rare occurrence. The use of Engler's Viscosimeter, which is prescribed in the official catalogue for petroleum residuums, in which the accuracy is mostly interfered with by the considerable adhesion of the substance to the walls of the opening through which it flows, is open to some criticism. The methods are better which rest upon the observed time at which a heavy body sinks in the material, which by being warmed approaches the melting point.*

"Aktien Gesellschaft für Teer-und Erdölindustrie" Method.—Reliable results are obtained by the use of processes worked out and named, which in the industry of the Aktien gesellschaft für Teer-und Erdölindustrie, have been generally introduced and for a long time and by a very great number of determinations, have been recommended. About 25 gms. of the pitch or asphalt under investigation are melted in a small tin vessel with an even bottom (Fig. 22) in an oil-bath of a form as shown at about 150°, the height of the molten pitch being about 10 mm. In this a glass tube open at both ends and some 10 cm. in length, is dipped in such a manner that 6 or 7 mm. of the tube are filled with the melted pitch; the other end of the tube is closed with the finger and the pitch in the full end is allowed to cool by revolving it horizontally in the air. As soon as the pitch will no longer flow, the pitch on the outside of the tube is removed. The

*Chem. Ind. 1903, p. 55; Köhler, 358.

height of the pitch in the tube should be, as a rule, about 5 mm. Upon this is placed 5 gms. of mercury which for this purpose may be measured in a marked tube. The tube is suspended in a Becker Glass full of water, which again is suspended in a second glass of water (Fig. 23). In the inner glass of water is placed a thermometer in such a position that the bulb thereof is at the same level as the layer of pitch in the tube. The water is now heated with a moderate flame. The temperature at which the mercury breaks through is noted as the softening and melting point of the pitch or asphalt.

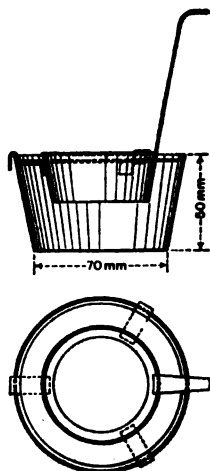


Fig. 22.

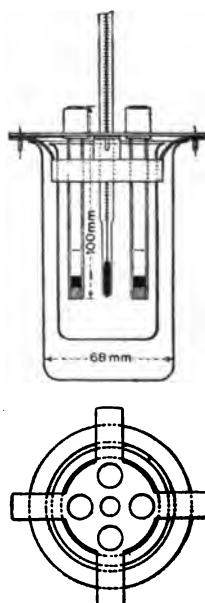


Fig. 23.

"Aktien Gesellschaft für Teer- und Erdölindustrie" method.

It can be readily seen that the apparatus as shown in Fig. 23, not only permits one but several tubes holding pitch or asphalt to be observed at the same time, so that the melting points of several samples can be taken simultaneously. For asphalt the melting point of which is higher than 90° , the outer Becker glass should be filled with paraffine oil, and the inner with a saturated solution of common salt or magnesium chloride.

The melting points found by methods heretofore employed differ by a few degrees; that is, they are so much lower. They are somewhat influenced by the diameter of the tube, the thickness of the layer of pitch and the height of the column of mercury. With like quantities of mercury (5 gms.), the increased diameter is compensated by the decreased height of the layer of mercury. As has been pointed out, the influence of the thickness of the layer of pitch within certain limits, is not noticeable. A layer of pitch of 5, 6 and 7 mm. in thickness gave 61.5°, 60.5° and 61.5° as the softening points.

As illustrating the reliability of the process, the following single determination of different localities is given:

Origin.	Soft Pitch. Degrees C.	Medium Hard. Degrees C.	Hard Pitch. Degrees C.
Grabow, Moravia	51.0	68.5	80.0
Grabow, Moravia	51.5	68.5	80.0
Grabow, Moravia	51.5	68.2	80.8
Grabow, Moravia	51.3	69.0	80.5
Niederau, Saxony	83.0
Niederau, Saxony	84.0
Pasing, Bavaria	83.5
Pasing, Bavaria	84.5
Erkner	50.0	61.5	87.0
Erkner	50.5	60.5	86.0
Erkner	51.0	61.5	87.0

A mastic block that gave in Grabow a softening point of 58°, likewise gave in Berlin 58°. Other different asphalts and asphaltic bodies were examined by the same process and also with the usual capillary method and gave the following results:*

	After Krämer and Sarnow. Degrees C.	By Capillarity. Degrees C.
Cerisin	52.0	47.0 to 53.0
Beeswax	55.5	61.5 to 63.5
Paraffin	46.0	45.0 to 48.0
Asphalt, refined, hard.....	51.5 to 52.0	Wholly indistinct
Asphalt B, glass, hard.....	82.0	Wholly indistinct
Petroleum residuum, Alsace petroleum.	105.0	
Colophony	67.0 to 67.5	

*Köhler, Chem. u. Tech. d. Nat. u. Kunst. Asphalte, p. 359.

FLOW.

This test as applied to different samples of solid bitumens is wholly empirical, arbitrary and relative. It consists in preparing cubes of about half an inch dimensions, of the material to be tested and also cubes of the same dimensions of any similar material that may be selected as a standard of comparison. A cube of each variety is placed in a warming oven supplied with a glass door, upon a glass plate inclined at a slight angle. A uniform source of heat is applied and the temperature and time noted at which the two cubes lose form and then flow down the plate. The length of the flow upon the plate is also noted.

The significance and value of the results obtained from this test depend wholly upon the selection of the standard specimen to be used for the comparison.

DUCTILITY.

This term has been used to designate those properties by virtue of which a metal can be drawn into wire. By analogy the term is applied to solid bitumens and designates the similar properties possessed by them in varying degree by which they may be extended without fracture. A bitumen that can be extended into long threads is said to be ductile. One that cannot be extended but breaks abruptly is said to be short.

Mr. A. W. Dow has contrived an apparatus by which he measures this property, which he describes as follows:

"The ductility of an asphaltic cement is determined by ascertaining the distance in centimeters that a prism of the cement can be drawn out before breaking. The size of the prism that I have adopted is one 5 cm. in length and with a square cross section of 1 cm. The molding of this prism is done as follows: Fig. 24 shows the four pieces which fit together to make the mold. Fig. 25 shows the mold put together for filling. Before fitting, the mold is put together on a brass plate, and to prevent the asphalt adhering this plate and the inner sides of the two pieces of the mold (a and á) are amalgamated. The asphalt cement to be tested is poured into the mold while in a molten state, a slight excess being added to allow for the shrinkage on cooling. After the asphalt cement is nearly cooled the prism section is smoothed off level by

means of a trowel, which should be wet with water to prevent its sticking. When it is thoroughly cooled to the temperature at which it is desired to make the test, the clamp and two side pieces are removed, leaving the prism of asphalt cement held at each end by the ends of the mold that now take the part of clips. The test is made by pulling the two clips apart at a uniform rate of speed by means of hooks inserted in the eyes. The prism should be kept in the freezing mixture or water at the temperature desired, and the test made while so immersed so as to insure the temperature remaining constant. The rate

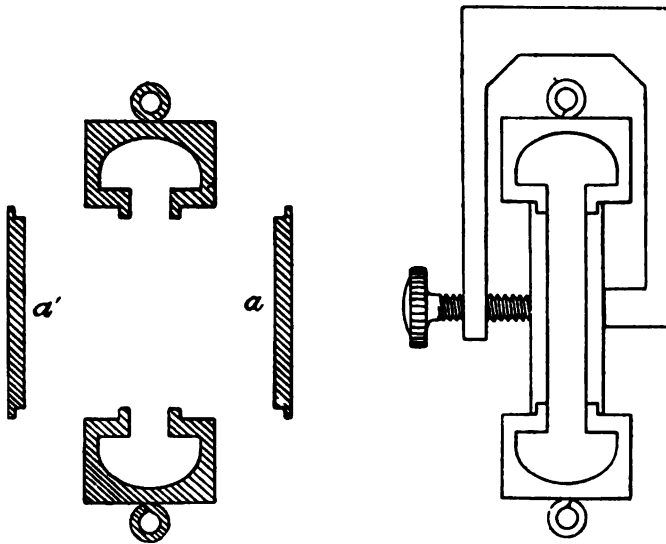


Fig. 24.

Dow's Ductility Apparatus.

Fig. 25.

of speed adopted for pulling the clips apart where the test is made at 77° F. is 5 cm. a minute, and 1 cm. per minute where making the test at 20° F. Up to the present time I have pulled the clips apart by hand, but am now working on a machine that will do this and at the same time measure the force required to pull the clips apart at the standard rate of speed."

PENETRATION.

A. W. Dow.

"The softness of an asphaltic cement is determined by ascertaining its consistency or penetration by means of the

penetrating machine, at 32°, 77°, 100° and 115° F. The rate of softening of an asphaltic cement is thus determined, and an idea can be arrived at as to whether it would be too soft for use at the maximum climatic temperature.

"The consistency or viscosity of an asphaltic cement is determined by ascertaining the distance that a standard needle will penetrate into it under a standard weight and in a standard interval of time. The distance that the needle penetrates is called the penetration of the sample. There are three types of apparatus all depending on the same principle, that of a needle penetrating, that have been described. The first ap-

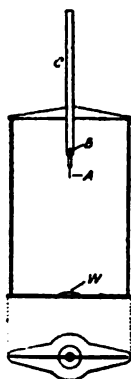


Fig. 26.—Penetration Needle

paratus was devised by Prof. H. C. Bowen in 1888 and is patented (Patent No. 494974). It is also described by Mr. Richardson in his report to the Engineer Commissioner of the District of Columbia for the year ending June 30, 1891, p. 106. The author describes still another sort of apparatus in the report of the Operations of the Engineer Department of the District of Columbia for the year ending June 30, 1898. This apparatus has been found very economical for experimental work, but being rather cumbersome to have in paving yards, etc., a simpler apparatus was devised which answers all purposes, even experimental work. The latter is shown in the accompanying figures, Nos. 27 and 28.

In Fig. 26 is shown the No. 2 needle, A, inserted in a short brass rod, which is held in an aluminum rod (C) by the

binding screw, B. The aluminum is secured in a frame work so weighed and balanced that where it is supported on the point of the needle A, the framework and rod will stand in an upright position, allowing the needle to penetrate perpendicularly without the aid of a support. The frame, aluminum rod and needle weigh 50 grams; additional weight, when desired,

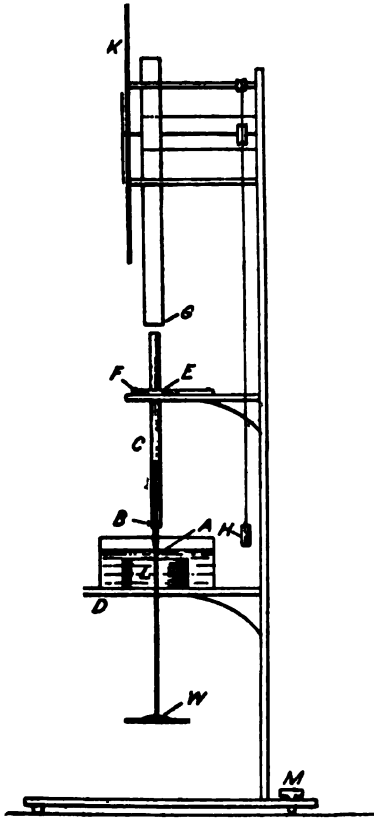


Fig. 27.

Dow's Penetrating Apparatus.

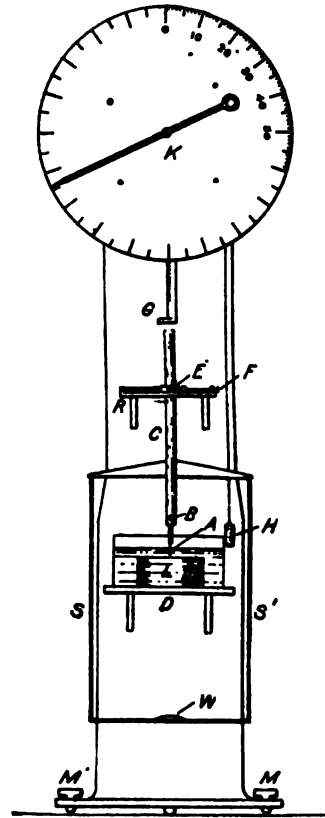


Fig. 28.

is placed on the bottom of the frame at W. In Figs. 27 and 28 are shown the side and front views of the entire apparatus put together and ready for making a penetration. D is a shelf for the sample. E is a clamp to hold the aluminum rod C until it is desired to make the test. F is a button which when pressed opens clamp E. By turning this button while the

clamp is being held open, it will lock and keep the clamp from closing until unlocked. The device to measure the distance penetrated by the needle consists of a rack, the foot of which is G. The movement of this rack up or down turns a pinion to which is attached the hand which indicates on the dial K the distance moved by the rack. One division of the dial corresponds to a movement of the rack of $1/100$ cm. H is a weight hung by a coarse thread which winds on a drum on the axle of the spindle and counterbalances the rack so that the rack can be raised or lowered by moving this counterweight H up and down. L is the tin box containing the sample to be tested, which is covered with water in a crystallizing dish, thus keeping its temperature constant, MM are leveling screws. Fig. 29 represents a clock movement having a 10-inch pendulum attached to the wall to one

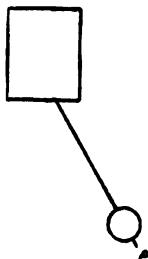


Fig. 29.—Pendulum.

side of the machine, used for timing the test. Make a mark, P, on the wall just at the extremity of the swing of the pendulum. A double swing of this pendulum—that is, from the time it leaves P until it returns—is one second.

“To make the penetration test, the samples of asphalt cement contained in circular tins, along with the glass, dish, are placed in a receptacle containing at least 5 ins. of water, which should have been previously brought to the temperature at which it is desirous to make the test. While the samples are under the water it should be stirred every few minutes, best with a thermometer, and the temperature kept constant when necessary by the addition of hot or cold water as the case may require. The samples should remain under the water at least fifteen minutes, and in cases when their temperature is not near that at which the test is to be made they

should be left in possibly half an hour. After the samples have remained in the water a sufficient time to have attained their temperature they are ready to be penetrated.

"One of the samples is now placed in a glass dish and removed in it, covered with as much water at the standard temperature as is convenient without spilling. The glass cup containing the sample is placed on shelf, D, under C, as shown in Figs. 27 and 28. Insert brass rod with needle into C, and secure by tightening binding screw B. Lower C until the point of needle very nearly touches surface, then, by grasping the frame with two hands at S and S', Fig. 28, cautiously pull down until needle is just in contact with surface of sample. This can be best seen by having a light so situated that looking through the sides of the glass cup the needle will be seen reflected in the surface of the sample. After thus setting the needle, raise counterweight slowly until the foot of rack G rests on the head of rod C; note reading of the dial. Place thumb of right hand on R and press button, F, with forefinger, thus opening clamp. Hold open for the desired time and then allow it to close. Raise counterweight H as before until foot of sack rests on rod C. The difference between the former reading of the dial and the present is the distance penetrated by the needle or the penetration of the sample. Raise rack, loosen binding screw B, raise rod, through clamp, having the needle sticking in sample. Remove needle from sample, clean well by passing through a dry cloth, replace needle in C, and the machine is ready for another test."

"The needle which I have adopted as a standard for penetrating is a No. 2, manufactured by R. J. Roberts, Redditch, England. All the needles, however, obtained in a package, cannot be used for penetrating, as they vary somewhat in shape, and only those are selected which give a penetration corresponding to a standard needle. The standards that I have adopted for this machine are at 32° F. or lower, the distance in hundredths of a centimeter that a No. 2 needle will penetrate into the sample in one minute of time when weighted with 200 gms.; for tests made at a temperature of 77° F., the distance in hundredths of a centimeter that a No. 2 needle will penetrate into the sample in five seconds of time when weighted with 100 gms. For tests made at a temperature of

100° F., or above, the distance in hundredths of a centimeter that a No. 2 needle will penetrate in five seconds of time weighted with 50 gms."*

I have given a description of this apparatus in Mr. Dow's own words.

This apparatus is of great value, especially in this improved form. It is chiefly valuable for comparison of different samples of the same kind of bitumen, under the same conditions. It will not indicate chemical stability and should be strictly confined to those physical properties that it indicates within its own limitations.

*Proc. Am. Soc. for Testing Materials, 1903, Vol. III, pp. 352-357.

PART IV.

**CHEMICAL TECHNOLOGY OF
BITUMINOUS STREETS.**

CHAPTER XVI. HISTORICAL INTRODUCTION.

Although asphaltum and other forms of solid bitumen have been used since the dawn of history, their general use as articles of commerce is almost wholly confined to the eighteenth and nineteenth centuries. Cisterns and silos that are lined with solid bitumen, said to be still intact, are found in Petrea and Egypt, and they must be from two to three thousand years old; yet, the manner of their construction, the locality from which the bitumen was obtained, and by whom they were built, can only be conjectured.*

In 1721, Eirinis d' Erynys, a Greek physician, published a pamphlet in Paris, France, in which he described the deposits of bituminous sandstone and limestone found at Val de Travers, canton of Neufchatel, Switzerland, in the upper valley of the Rhone. He compares these deposits of bituminous rock with similar beds that occur in the valley of Siddim near Babylon. These deposits were forgotten for nearly a century and then rediscovered.

I have sought in vain for any record of the person who first suggested the use of this material for paving. The idea was no doubt original in more than one locality, as I have discovered traditional evidence that in the valley of the Rhone, in Trinidad and in California, it was observed that the fragments of asphalt that were jolted from carts, were crushed and compacted into a solid rock bed, by the wheels of the carts that followed. The conviction that other road beds could be constructed of the same material was inevitable.

In 1797, the French government made a concession to M. Secretan of all country between Seyssel and Belgarde on both sides of the Rhone, fourteen miles in length by one and one-half miles in width. This concession was in litigation fifty years.

In 1834, Puvis described the methods employed at the

*Paving and Munic. Engineering, x. p. 381.

Seyssel works, for extracting the bitumen. He describes the sandstone as containing from 2 to 3 per cent and the limestone as much as 9 per cent, of bitumen.*

In 1850, M. De Coulaïne published a very important paper, in which he discussed bituminous rock streets in a manner that in the light of our present knowledge and experience appears very remarkable.†

"The Annals of Bridges and Roads" is a publication issued by the French government, containing reports by the different engineers having in charge the public roads of France, together with memoirs upon subjects pertaining to the construction and maintenance of bridges and roadways. It is a work of the greatest value, very little known to the general reader.

He states that the first attempt to construct a street of bituminous rock in Paris was made upon the Place Louis XV, opposite the church of Saint Roche. This pavement was about 0.15 m. (6 in.) in thickness, and was formed of fragments of quartz and of mastic of coal tar (*bitume de houille*) upon a bed of sandstone, the joints of which were filled with mastic. No date is given. These coal-tar streets, even with a concrete base, were not satisfactory.

De Coulaïne discussed bituminous mastics at length and insisted that they should consist of mineral tar and lime, to which sand and gravel may be added, but the choice of the tar and lime are alone of importance.

He says, the tars melt completely at a little above 100° C. and give off vapors and boil at 120° to 140° C. As the distillation progresses, the liquidity and elasticity of the bitumen diminishes, until finally there remains a brilliant black substance very brittle at the ordinary temperature and decomposed with great ease by prolonged heating. He says, the natural tar of Bastennes is quite different from coal-tar, which evaporates more rapidly, producing a brittle mastic, while the oils of the natural tar remain "fixed." He further states that sulphur made the mastics brittle, and observes that when lime is used in the preparation of mastic, it is preferable to use quick-lime reduced to an impalpable powder.

**Annales des Mines*; 3d Series; Vol. vi, p. 179, 1834.

†*Annales des Ponts et Chaussées*, 2d Series; Vol. xix, p. 240, 1850.

He prefers the bituminous rocks found at Seyssel, Val de Travers and Lobsann, which are composed principally of carbonate of lime and bitumen, completely identical with the tar (*maltha*) of Bastennes, generally mingled in the proportions, nine parts of mineral to one of bitumen, as great difficulty was experienced in effecting a complete mixture of the tar and quicklime. He asserts that it is indispensable that the mastic fill such conditions that when used it will not be so hard as to lead to fracture, nor so soft as to receive impressions from heavy traffic. Another matter of importance is the concrete base, which should be thick enough to be unyielding, and also that the proper season in which to lay bituminous rock streets is from May 1 to September 15.

A careful examination of this paper shows that at its date, November 30, 1849, ten years' experience with bituminous rock streets had demonstrated the following points:

That coal-tar was unfitted for the construction of streets.

That quicklime in impalpable powder is to be preferred to a grit, however fine, made of pulverized limestone.

That the natural bituminous limestones are superior to any artificial mixture of lime and bitumen either with or without sand.

That for such purposes as require an artificial mastic, Bastennes tar or *maltha*, deprived of its light oils, is the best material with which to soften Seyssel rock.

That manipulation is of more importance than choice of materials, and that prolonged heating and overheating are especially to be avoided.

Although De Coulaïne nowhere uses the word *maltha*, he repeatedly uses the term mineral tar (*goudron minérale*), which is the equivalent for *maltha* as used by many other authors.

In 1865 it was generally understood on the Pacific coast that the natural bituminous rock found at La Goleta, near Santa Barbara, Cal., containing about 50 per cent. sand, furnished a better material for paving than could then be made of any artificial mixture of sand with the purer asphaltum of that region.

In the same volume with the paper of M. De Coulaïne is the report of M. Ledun upon the "*Asphalte of Auvergne*,"

who laid a piece of what he calls "bituminous macadam" on the road from Paris to Perpignan in the department of Clermont-Ferrand. The report is dated February 29, 1852. This road was covered with crushed (molasse) natural bituminous sandstone, and compacted by use after the manner of an ordinary macadamized roadway.

In 1861, M. Leon Malo, who had not long before been made the manager of the works at Seyssel, where bituminous limestone is mined and mastic prepared from it, published a memoir also in the *Annales des Ponts et Chausses*, which has since been published in book form and has become a classic upon this subject.*

He says, the rock is prepared for use either by crushing cold or by decrepitation. When treated by the first method it is afterwards heated in retorts and mixed with hot bitumen to form mastic. When treated by the second method it is heated on iron plates. Or, it is heated in an apparatus analogous to a large coffee roaster, which, worked by suitable gearing was fed at one end and discharged from a trap near the other. The bitumen softens, and the mass falls to a powder which is sifted. As the powder cools slowly, it is carted from the decrepicator to the street in one-horse loads, which are spread by the workmen with rakes completely across the street. It is then rolled until cold. Nothing can exceed the simplicity of the operation.

For the preparation of mastic the rock is crushed in a mill resembling a huge coffee mill, and heated on revolving cylinders, and thrown hot into pure bitumen heated to near its boiling point. The hot rock decrepitates, and a very intimate mixture is formed, which, after being heated and agitated during six hours, is allowed to cool in circular molds, forming masses in shape like a cheese. This mastic is strong, easily fusible and different from the original material. "Whatever be the action of the bitumen added, it is a constant fact that the closer the geological analogy between it and the bitumen with which the rock is impregnated the better is the mastic obtained."

He condemns the use of candle-tar, coal-tar, and all other

**Annales des Ponts et Chausses*, Series 4, vol. 1, p. 69, 1861. *L'Asphalte: Son origine, sa preparation, ses applications*, par Leon Malo, Baudry & Cie, Editeurs, 15 Rue des Saints Peres, Paris.

refuse material, in place of the pure natural bitumen, and remarks, "that combination which is sought to be imitated in a cauldron by a mixture of a solid and liquid body without affinity for one another, is in the natural asphalt the result of one of those colossal operations of nature that man is interdicted from repeating."

I wish to emphasize the conclusions reached by this eminent observer:

That the bituminous limestone of best quality consists of a fine grained rock, in which each particle of mineral matter is enveloped, and separated from its neighbor by a cushion of elastic, adhesive bitumen.

That want of care in heating the rock injures or destroys its valuable qualities.

That in the preparation of mastic, the rock should be softened with natural bitumen as nearly as possible of the same kind and quality as that originally contained in the rock.

That all attempts to prepare a substitute or artificial mastic of asphalt and coal-tar, or any other refuse material of similar nature had signally failed.

These conclusions were reached at the beginning of 1861.

During the following twenty years streets were laid in Paris, London and other European cities, generally with satisfactory results. In 1880 William H. Delano, in London, Eng., read a paper before the "Institute of Civil Engineers" which provoked a lengthy discussion, to which further reference will be made.

The consensus of opinion reached by this symposium may be stated thus:

That beginning at the bottom clay is a very bad foundation for a street.

That sand is but little better, both when wet throwing the concrete and asphalt, when invaded by frost, and therefore requiring to be drained.

That lime mortar is worthless under asphalte.

That hydraulic cement or lime is better, but not good.

That 4 ins. of Portland cement concrete will sometimes answer, that 6 ins. is usually good, while 9 ins. under any circumstances will stand indefinitely.

That Seyssel or Val de Travers asphalté well laid, on a good concrete, well dried, is uniformly a success; that laid on a concrete deficient in either thickness or quality of material, they will fail.

That any asphalté may be ruined if overheated or laid on wet concrete.

That as very good streets have been made of almost every asphalté known, it is fair to conclude that a good street depends more upon the materials and technique of the concrete, and in the care and skill exercised in laying the asphalté, than in the locality from which the asphalté is obtained.*

The word "asphalté" in the above conclusions signifies the natural bituminous limestones found at Seyssel and other localities in Europe only.

"ASPHALT STREETS."

No very considerable amount, of what are known in Europe as "asphalté streets," have been laid in the United States. In several cities of the Atlantic Coast, streets and squares have been, for various reasons, covered with imported Seyssel Rock. These constructions have usually been satisfactory in all respects except cost, which of necessity must be high, as compared with so-called sheet asphalt streets. The fine quality and durability of these constructions has very generally stimulated the desire to discover similar deposits on this side of the Atlantic. While bitumens in great variety are widely distributed over the North American continent, the bituminous limestones and dolomites that resemble the rocks found at Seyssel and Neufchatel have been discovered but sparingly. An extensive deposit was reported some years ago to exist in Michigan, but nothing has been heard of it commercially. In the southern central part of Oklahoma, in Carter county, a few miles west of Ardmore, and farther north and east of Dougherty, in Murray county, very extensive deposits of bituminous, dolomitic chalk, soft and easily quarried, have been quite largely used for streets in Kansas City, Ardmore, Fort Worth and other cities of Texas.

*Minutes of the Proceedings of the Institute of Civil Engineers, Vol. xliii, p. 276, 1876. Ibid. Vol. lx, p. 109, 1879-80; Paving and Municipal Engineering, Vol. xi, p. 67, 1896.

The rock has not been treated in the United States as it has been treated in Europe, nor is it used alone, but it is mixed in certain proportions with the bituminous sands and sandstones, that are found in the immediate neighborhood of the limestones. For the Kansas City streets the two kinds of bituminous rock were ground together and mixed into a sort of mastic, at the mines, and transported to the street in large cakes that were melted and laid upon the streets. I have lately been told by persons familiar with the streets of Kansas City, that these asphalt streets, some of which were laid seventeen years ago, are now in just as good condition as when laid. These streets of bituminous rock exhibit a very marked superiority over the so-called sheet asphalt streets that have been laid in the same city.

In Ardmore, a number of streets have been laid in a manner more nearly approaching the method pursued in Europe. The material used was taken from quarries a few miles south of Ardmore, and were thoroughly mixed after being softened by heat. The material was spread on a concrete foundation, without a binder, and rolled until cold. When I inspected this street on one of the hottest days in August, it was solid as a rock. Neither horse's hoofs nor wagon tires made the slightest impression on it. I said to the City Engineer, You have very few six-ton loads on this street; he replied, no, but we have traction engines, with corrugated wheels, and they do not make the slightest impression on it. I am told there are many others like it in the cities of northern Texas. I know of no such streets in any Atlantic or Pacific Coast city. They are the product of the intelligent application of sound principles of technology, to the manipulation of the best materials for the construction of solid bituminous streets, yet found on the American continent.

Natural roads of asphaltum, for short distances, had been known in southern California prior to my first visit there in 1865, for an immemorial period. It was only a step from those to streets of asphaltic mastic, as there was an abundance of material with which to construct them at tide water on the coast above Santa Barbara.*

*Geol. Survey of Cal. Geology, Vol. II, Appendix, p. 60, 1882.

I doubt if anyone now knows when this material was first used there for pavements. When I visited the locality in 1866, I was told that the natural bituminous sand containing about 50 per cent. of very fine quartz and pulverized shale, was much to be preferred to any artificial mixture that could then be prepared from a purer asphaltum and sand. Methods for mixing asphaltum and sand have been greatly improved since 1866. Streets have been laid in the Pacific coast cities of bituminous mastic made with both the bituminous sandstone and asphaltum, with varying success. Frost does not trouble them in that region, but the streets have, in some instances, been spoiled by laying in wet weather and from other causes. Having again visited that region in 1894, I am prepared to testify that the technology of asphalt paving, that has grown up there locally, has resulted in giving San Francisco, Santa Barbara, Los Angeles and other cities as good bituminous avenues and streets as are to be found in the average American cities.

There is no doubt that De Smedt laid the first bituminous mastic street that was laid in any Atlantic coast city, in front of the city hall in Newark, N. J., in 1870. He was a Belgian by birth and had learned the technique of bituminous rock pavement in Paris before he came to the United States in 1861. He ought to have known all that De Coulaire and Malo knew before he left Paris. There was no bituminous limestone, good or bad, to be had on the Atlantic coast. Even Trinidad pitch was very little known at that time. The Grahamite of West Virginia and Albertite of New Brunswick, with Cuban Chapapote, all nearly pure, hard and dry asphaltums, and of high cost, were practically all of the bitumens then available. There was no natural maltha, resembling Bastennes tar, to be had at any price, with which to soften these asphaltums. The only materials at hand were coal-tar, well known to be unsuitable, and the refuse of the petroleum refineries, that thirty years' experience in Europe had then proved to be but little better.

It would be interesting to know the details of the history of De Smedt's first pavement, just what went into it and how long it lasted. Between March 1, 1870, and February 7, 1871, De Smedt took out several patents. An examination of these

patents shows that they cover the application of a well known process, which De Smedt must have learned in all its details in Paris, to new materials such as were then on the market in the eastern United States. It is not likely that he used either the expensive Grahamite or Albertite; he probably used Trinidad pitch and petroleum residuum—the same materials that have since been used.

Soon after, the successful laying of bituminous surfaced streets in Washington, D. C., led to their general use throughout the country.

CHAPTER XVII. A MODERN STREET.

A modern street consists of a concrete foundation upon which is placed a wearing surface to protect the concrete. The wearing surface may consist of bituminous rock, bituminous mastic or cement, bituminous block or wood block, or brick with bituminous joints.

THE FOUNDATION.

A suitable unyielding foundation should be constructed whatever may be the surface selected. The primary importance of an adequate mass and quality is self-evident.

In a paper published in 1880, W. H. Delano discussed at some length the proper foundation for a bituminous rock street. He says, "The tradition is that sand is incompressible, that sand makes a good foundation for granite sets, and therefore does equally well for concrete. Sand is incompressible in a cylinder, but under street traffic gets displaced and absorbs water, causing the concrete to crack. The bituminous layer follows and then unsatisfactory repairs are made, for repairs on a shifting concrete, through which the wet can rise, never last long."

"In preparing the road of the Auteuil Bridge, Paris, a coating of liquid asphalt $\frac{5}{8}$ in. thick was laid down to keep out the surface water from the masonry, then a 3-in. bed of sand by order of the government engineer, who feared lest the immediate contact of the rough concrete with the bituminous mastic would damage this coating. On the top of the sand was put a layer of hydraulic lime concrete, and on top of the concrete 2 ins. of compressed Val de Travers bituminous limestone. The rain water filtered through the curbstone into the layer of sand; in hard winters it froze and forced up the concrete, and in summer the sand yielded under heavy traffic. In 1877 the roadway of the Pont Masséna, Paris, was laid. Nine inches of Portland cement concrete was placed upon the liquid asphalt coating, and upon that $2\frac{1}{4}$ ins. of compressed

Val de Travers bituminous limestone. It never moved, though subjected to heavy traffic." In 1875 the flooring of the Elbeuf bridge, Paris, was repaired. "This structure is of wrought iron, subjected to considerable vibration. The flooring is of Mallet's buckle-plates. Owing to the shape of the buckle-plates the hydraulic lime concrete was of unequal thickness, broke up under the vibration, and the asphalt of course followed. To meet the difficulty of the vibration, it was resolved to replace the hydraulic lime concrete with bituminous concrete. The roadway was accordingly taken up, the old compressed bituminous limestone was heated until it fell to powder; it was then mixed with refined bitumen to make it into a mastic, to which 40 per cent of dry grit was added, and with every 2 parts of this asphaltic mortar, 3 of hot flintstone were mixed. This concrete was laid down hot upon the buckle-plates, and well rammed and dressed till a hard and slightly elastic surface was obtained. Upon this surface a layer 2 ins. thick of compressed Val de Travers bituminous limestone was put down. The work was finished in October, 1875. Up to August, 1879, not a single repair had been made."

A lengthy discussion followed Mr. Delano's paper. Mr. E. J. Harrison said that, "the first bituminous limestone roadway laid in the city of London, was laid in Threadneedle street in 1869. It consisted of 2 ins. of compressed Val de Travers bituminous limestone on a concrete foundation." It was, at the time he spoke, "within two months of 11 years old, and was then, as it always had been, in good condition." He said further, "he had been struck with the unanimity with which every speaker urged the necessity of a solid foundation for a good road. A bituminous limestone road was in reality a concrete road with a surface of bituminous limestone put upon it to carry out certain ends. If the concrete foundation were taken away or tampered with, or negligently laid, bituminous limestone itself would form a very sorry paving. For that reason, his company had always urged the desirability of laying a concrete composed of a quick-setting Portland cement with the best obtainable ballast. The only failure he knew in Val de Travers roadways had been in the use of lime concrete under lime mortar, in Holborn opposite Gray's Inn. The specification prescribed about 9 ins. of lime concrete

with $\frac{3}{4}$ in. of lime mortar. When the concrete was ready to receive the bituminous limestone, a fire broke out in Holborn, the place was flooded with water, the engines drove over the concrete, and the population of Gray's Inn trampled it down. It was subsequently made good and the bituminous limestone spread. For five or six years the road was kept up at considerable expense, and then relaid. On removing the bituminous limestone, it was found that the lime concrete had never set, that the mortar floating had never adhered to the concrete but was mostly in powder, produced by the action of the rammers or by traffic afterwards."

"Reference was made by several of the speakers to cracks both in the compressed bituminous limestone and the mastic. They were generally attributed to defects in the concrete, arising from various causes. They usually appear in severe weather. Coarse sand in mastic is objectionable and causes disintegration. Chabrier noticed that cracks appear in work laid in wet weather. Delano observed that if mastic was placed on wet concrete it would blister and sometimes crack. He believed that cracks in nine cases out of ten resulted from the concrete."

Mr. Fogarty was of the opinion that if the concrete was laid almost dry and thoroughly rammed and jointed at intervals, the joints being left open until the water had evaporated, it might be covered with bituminous limestone without any fear of cracks, provided there was a solid substratum. But when it was laid upon clay, difficulties would invariably arise unless there was interposed between the concrete and the clay a considerable amount of hard, pounded, dry filling for drainage purposes. The most difficult pavements were those laid upon a clay substratum, and he knew of no mode of curing the difficulty except by getting out a considerable depth of clay and replacing it by dry material."

"Other causes of disintegration are due to deficient ag-
gregation, which may arise from two circumstances, either the powder has been too cold when laid, or it has been overheated. Overheating bituminous limestone renders it as inert as sand. It is quite possible to make bad work with good materials, though the converse is not true. Still, when good bituminous limestone, properly prepared, and laid by skillful workmen,

does not stand, it is almost always the fault of the concrete."

The consensus of opinion reached by this symposium was stated on page 285. The gentlemen who expressed these opinions represented the experience and skill that had been gained by thirty years' practice in laying streets with Val de Travers and other bituminous limestones found in Europe. In the long quotation given above the word "asphalte" was used to designate these bituminous limestones which fall into a powder when moderately heated, that may be passed through a screen while warm without clogging the screen.

This word "asphalte," spelled with a final e, is not equivalent in meaning to the word asphalt, used in the United States. Nor is any material called asphalt in the United States identical with the bituminous limestone called "asphalte" and found and used in Europe. It is nevertheless a fact, that the consensus of opinion reached by these eminent and experienced technologists, applies equally to the foundations laid in the United States and to the surfaces prepared from natural solid bitumens, that have been laid upon them. It may be generally stated that good streets have been constructed from every kind of natural solid bitumen that has been used for the purpose. No such general statement can be made concerning the so-called "artificial asphalts" that have been named on a previous page (see page 204). It is quite certain that some of them are wholly unfitted for use in the construction of streets, and it remains to be proved that any of them are equally good when compared with natural solid bitumens. Excluding the so-called artificial asphalts that have been used in the United States as being uniformly of very varied and uncertain quality, the consensus of opinion reached by the symposium as stated on page 285 may be affirmed with equal force as being fully sustained by the experience gained in the United States, since 1880.

Indeed, it may be truthfully stated that successful street construction, no matter with what material the surface may be laid, on a concrete foundation, depends primarily on the stability and permanence of the foundation. The cement should be Portland cement of the best quality. No small economies should be thought of in this connection. No specious arguments that cheaper cements will, in time, set as

strongly as Portland cement should be allowed a moment's expression. The first load that enters upon the street may be a maximum load of coal. Its entry cannot be delayed. It is no adequate test that the street is rolled with a 10-ton roller 48 ins. wide giving about 250 lbs. per lin. in. A 6-ton load of coal in a modern wagon is two-thirds on the hind wheels, which may have a rim each 4 ins. wide, putting 8,000 lbs. on 8 ins., or 4 times 250 lbs. to the lin. in. Nor for the same reason should any 4 in. concrete be laid, nor surfaces be put down on old Belgian blocks, rolled with a 48-in., 10-ton roller. Six-ton loads of coal test the stability of every street in our large cities, no matter whether they be residence streets or not. If 4-in. concrete or unstable Belgian block gives way under such a test the bituminous surface is sure to follow and a hole in the surface or both surface and foundation is sure to come in time. Inadequate foundations are also responsible for no inconsiderable portion of the damage from leaky gas mains and from the ascent of substructure water. To insure good streets the concrete foundation should be 6 in. thick, rigid, stable and impervious, hence cements that make weak and spongy mortars should be uniformly discarded.

Clean, sharp, hard sand of properly assorted sizes to fill all the voids is an essential element in a first-class concrete. Mr. Clifford Richardson, in his *Modern Asphalt Street*, page 28, has discussed the subject of sand in a manner that leaves little or nothing to be said. The reader is referred to his pages which are outside the purpose of this work.

The stone should be clean, unweathered rock; it matters little of what kind, so long as it is hard and free from weathered portions, that are easily disintegrated. The presence of rock masses that will crush more easily than the cement mortar, contributes to a weak concrete, even with the use of a first-class cement mixed with a first-class sand.

There is no reason for supposing that a street foundation made of suitable materials and laid of proper thickness on a well drained substratum is subject, after complete setting, to deterioration or decay, if left undisturbed. The most potent cause of apparent failure of foundations, is street openings that have been carelessly or inadequately repaired. These openings frequently extend into the hitherto undisturbed sub-

soils of the street, and involve a large part of its permanent stability. If they are not replaced as permanently solid as the original soil, a slow yielding of the support of the foundation until the foundation bridges open spaces, or follows the settling of the soil, is certain. The failure of foundations and surfaces after street openings inadequately filled and carelessly repaired, is inevitable, and any surface, no matter of what material, will sooner or later follow such a foundation.

SURFACES.

The laying of surfaces of bituminous rock, chiefly limestone, as carried on in Europe, has been fully described in previous pages. In the United States so-called asphalt streets are laid with materials that require a technology in some respects quite different. The crude bitumen most frequently contains mineral or organic impurities, sometimes both, that have to be removed by refining. This is accomplished by slowly melting the bitumen at a low temperature and skimming the surface while the mineral matter is allowed to subside. The refined material is drawn off above the semi-solid "bottom."

The care with which this process of refining is conducted and the technical skill exercised are very important factors in determining the quality of the street surface that will be constructed from the refined bitumen. Too much attention has been paid to the rival claims of the owners of different deposits of natural bitumen and too little to the purely scientific questions involved, which are often fundamental and common to all varieties of bitumen alike. The technique employed by the engineers and the superintendents of paving plants where bitumens have been refined and paving mixtures compounded in the United States, like that employed by the masters of the art in Europe, as described by those masters for more than fifty years, consists of processes governed for the most part by "rule of thumb." The details of the work performed in London and Paris, at a cost of thousands of pounds sterling and millions of francs, much of which has been repeated in the United States at similar cost, exhibits an amazing disregard of principles that appear to be fundamental. How engineers trained in the best technical schools of the world could

expect a lime concrete to set out of contact with the external air; or porous concrete made of natural cement and only 4 ins. thick, too protect or sustain 2 ins. of bituminous mixtures; or any such structure, of whatever quality, to be made to stand over wet clay or sand invaded by frost, is simply marvelous.

However, "rule of thumb" is primarily based on fundamental chemical laws, that we may be too ignorant or too heedless to recognize; yet, which, in their invariable action, make precedent and routine possible, and lend to methods learned by experience that exactness that makes empirical technology possible. It is true such knowledge is gained at enormous expense, but the great cities of Europe and America have paid the bills. The trouble is easily determined by perusing the papers from which I have quoted. The experience gained since 1843 is to-day just as heterogeneous a mass of empirical knowledge as it was in 1850 when De Coulaïne published his little known, but valuable and interesting, paper, which seems to be unknown to the engineers of the United States. Not even a qualitative analysis, reaching final results, has been published, had upon any variety of solid bitumen known to the writer. No intelligent connection of mistakes has been made and but few standpoints have been gained from which one could reach out after more accurate knowledge. Conclusions have been reached and expressed as matters of opinion, almost as many and variable as the individuals expressing them.* It is therefore somewhat difficult to discuss from a scientific standpoint the practice that is followed in refining the different bitumens on the market. Considerations of business competition prevent any public demonstration of whether or no a hard and dry asphaltum heavily fluxed in refining, or a bitumen less hard and dry and moderately fluxed or a soft bitumen not fluxed at all, is the most desirable refined material with which to prepare asphaltic cement, as proved by actual use. Several facts appear, however, to be generally admitted by those most conversant with this technology. First, that in the preparation of refined bitumen or of asphaltic cement the bituminous flux shall be as free as possible from both solid and liquid paraffine. Second, that the bituminous flux shall be so completely blended with the solid bitumen

*Paving and Municipal Engineering, xl, p. 218.

that when the melted mass shall be poured into water no separation and floating of the oil shall take place, nor when broken into fragments or slices should they produce an oil stain on paper. Third, that the conclusion reached by De Coulaïne in 1850, is perfectly sound to-day, "That for such purposes as require an artificial mastic, Bastennes tar or maltha, deprived of its light oils, is the best material with which to soften" any form of solid bitumen. As a substitute for natural maltha, which is not everywhere available, the tar or dense residuum of the petroleum refineries is most frequently used. This residuum is a product of a variety of processes as carried on in different plants where different kinds of petroleum are treated. There is great choice among them. The best is none too good and the poorest may safely be rejected as too bad; the selection should always be made of that material that most nearly approximates in its qualities a natural maltha and will most completely blend with the solid bitumen to be fluxed.

The above remarks apply with equal force to the refining of crude solid bitumens and also to the conversion of the refined bitumen into so-called asphaltic cement.

The bituminous mastic that is laid upon the street is made by fusing together asphaltic cement, stone dust and sand. The stone dust should be hydraulic cement or air-slacked quicklime sifted through a No. 10 sieve. If a cheaper article than quicklime is desired, finely powdered limestone should be used in preference to quartz, granite or trap rock. Limestone or, more especially quicklime, will correct any acidity in the bituminous surface mixture arising from any cause. Limestone, not carbonate of lime should be specified, as powdered white marble, which most nearly approximates carbonate of lime, is never used.

Again De Coulaïne's conclusion "That manipulation is of more importance than choice of materials, and that overheating and prolonged heating are especially to be avoided," holds good to-day as in 1850.

The French engineers had reached the conclusion that those streets should not be put down in wet or freezing weather. The water in and upon wet concrete remains hermetically sealed beneath the bituminous sheet and perma-

nently prevents any adhesion between the two surfaces. The surface becomes very hot in summer and the confined water expands and some of it passes into vapor causing the soft and yielding surface to buckle and slide on the surface of the concrete.

I have never been convinced that a binder course filled with cavities, into which traffic soon forces a portion of the surface mixture, is an essential or desirable element of a bitumen surfaced street.

I wish here to particularize the construction of two exceptionally good streets that have come under my personal observation.

On visiting Washington, D. C., some years since, I made a careful examination of the general condition of the bituminous surfaced streets of that city. They have a deservedly very high reputation. A. W. Dow, then Inspector of Asphalts and Cements for the District of Columbia, showed me miles of the fine streets of the city and gave me such information as I desired. He told me he allowed the use of natural cements for concrete foundations, although his principal assistant (who has since succeeded him) admitted to me that Portland cement made a stronger concrete, that is more solid and less likely to be penetrated by water from the subsoil. He also allowed the use of petroleum residuum from the western refineries and residuums made from California malphas and petroleums for fluxing natural asphaltums and Trinidad pitch. I asked him if he had allowed the use in Washington of any solid residuums of any kind of petroleum under the name of asphalt or asphaltum, and he replied that he had not. He showed me a few very old streets, that were the first, or among the first, bituminous streets laid in Washington. They were made of a preparation of coal-tar pitch and coarse gravel, which was laid very thick, forming a sort of bitumenous concrete. They were in fairly good condition though more than twenty years old. Among these streets I noticed Vermont Ave., from H St. to I St., laid of Trinidad pitch by the Cranford Co. in 1880, on a foot of this old bituminous concrete. The bituminous base was so thick that no moisture could get through it to the surface. Although 22 years old it was in excellent condition.

Several streets in bad condition also lent their testimony. Sixteenth St. N. W., had been down for 21 years, laid by A. L. Barber in 1881, was nearly one-half in broken patches worn down to the concrete base. Fifteen-and-one-half St., between the White House and the Treasury, had been down 8 years; Trinidad Lake pitch on a concrete foundation. The ground is springy and moist, and the surface was disintegrating from the action of water on Trinidad pitch. On Executive Ave. the surface was laid of Trinidad Lake pitch. It had been down three years and was rapidly going to pieces (1902). According to Mr. Dow's report for 1899, "This pavement was laid on bituminous base (1889) and went to pieces very rapidly, owing to the springy nature of the ground. In 1894 it was taken up, the ground underdrained, and asphalt on hydraulic base laid; the hydraulic base was paid for by the District, the surface laid by Barber Co. free of cost." Mr. Dow assured me that no Bermudez asphalt surface laid in Washington had ever "rotted," not even in the gutters.

One of the best bituminous surfaced streets ever laid in the United States was laid on Franklin Ave., Buffalo., in 1879. "The specification was 6 ins. of broken stone, rolled with a 10-ton roller, 3 ins. of binder composed of gravel and coal-tar pitch, 2 ins. of asphalt surface composed of sand, Trinidad asphalt and fine ground limestone. The asphalt was fluxed with what was known as paraffine still wax, or wax tailings, which come from residuum of petroleum distilled and was of a greenish yellow color. The proportions of mixture were about as follows: To a $\frac{1}{2}$ cu. yd. box of hot sand (added to the sand before heating was $\frac{1}{8}$ part of fine limestone) I mixed 25 gallons of asphalt and wax, which had been combined by a stone agitator. The wax was $\frac{1}{8}$ part of the 25 gallons. The mass was roughly mixed by hand and then put through a long pug mill steam mixer—this being before the modern improved mixer had been invented. The heat of materials was kept as near as possible to 350° and was carted about $1\frac{1}{2}$ miles, and spread and laid at a heat of 250° to 300° . The limestone was screened by screening crushed stone, there being no facilities for grinding fine. The result was a large percentage of particles from $\frac{3}{8}$ in. down. These in after years showed plainly on the surface, but were held firmly in the

asphalt. We guaranteed the pavement for 5 years and there was no repairs required at the end of that time. The original pavement remained until a year or two ago, and has been considered the best wearing pavement in the United States, so much so that several competitors have claimed it as their pavement. In 1895 I inquired of the Buffalo city engineer about the record of the pavement and he reported as follows:

Laid in 1879—square yards, 7,264.	
Repairs, 1887	\$ 70.00
Repairs, 1888	196.23
Repairs, 1890	600.00
Repairs, 1891	115.16
Repairs, 1892	702.16
Repairs, 1893	246.20
Repairs, 1894	560.89
Repairs, 1895	340.75

\$2,831.39

Total cost for repairs per square yard\$0.403

Average cost for repairs per square yard per year, 16 years.. 0.25

Considerable repairs necessary. He considered the service of the street remarkable. * * * In 1878 I laid the intersection of Jones and Eddy Sts., San Francisco, using California asphalt with wax mixture. I saw the pavement a year ago and it was in good condition."*

These streets will be further discussed in succeeding pages.

*Letter from N B. Abbott, under date Sept. 19, 1898.

CHAPTER XVIII. BITULITHIC STREETS.

The foundation for the bitulithic pavement should be made after careful examination of the character of the subsoil or material over which the pavement is to be laid. If the subsoil is of a character, such as gravel, which can be rolled, a bituminous base is recommended. If the subsoil is spongy clay, or other material which cannot be rolled so as to provide a solid sub-foundation, a hydraulic concrete foundation is necessary.

Where the street to be improved is now paved with macadam, stone blocks, cobbles or brick, on either a concrete or other suitable foundation, and the grade of the street will permit raising the grade about 3 ins., surfacing with bitulithic over the present pavement is recommended. The foundation of asphalt or other pavement may readily be resurfaced with bitulithic wearing surface, by taking care to thoroughly roughen the old smooth surface of the concrete by hand picking or other means.

The sub-foundation having been thoroughly rolled, the bituminous foundation for bitulithic pavement is made of broken stone or slag laid to a depth of from 4 to 6 ins. or possibly more, according to the character of the subsoil and the traffic to which the pavement is subjected. The stone or slag is thoroughly rolled with a steam roller and then upon it is spread a heavy coating of bituminous cement. Or, an hydraulic concrete foundation is mixed and laid in the ordinary way from 4 to 6 ins. in thickness, depending upon the strength of the sub-foundation. A concrete 6 ins. thick, made of the best Portland cement is recommended. In order that the bitulithic surface may bond with concrete foundation, it is very important that the surface of the concrete be roughened after it is thoroughly tamped, but before it has become set, by spreading over the surface clean, broken stone that will pass a 2½-in. ring and remain on a 1½ in. ring. This should

be tamped for about half its depth into the fresh mortar. Then tamp with a small tamper (2 x 3 in.) with which depressions from $\frac{1}{4}$ to $\frac{1}{2}$ in. can be made in the concrete. It will be readily seen that this method provides a rough surface to the concrete, affording a union with the bitulithic surface which smooth concrete would not provide.

Before laying the bitulithic surface the concrete is carefully swept. A considerable portion of the stone tamped into the concrete will then become loosened and its removal will leave depressions in the concrete into which the bitulithic surface mixture will be impressed; the depressions thus formed giving the same advantages as the protruding particles of stone where they remain imbedded in the concrete.

Upon the foundation is spread the wearing surface which is compressed with a heavy steam roller to a thickness of 2 ins. The surface mixture is made of the best stone available, varying in size from a maximum of 1 or $1\frac{1}{2}$ ins. down to an impalpable powder, the various sizes of smaller stone, sand and impalpable powder being provided to fill the spaces between the larger stones. The proportions used of the various sizes of material are predetermined by physical tests with a view to obtaining the smallest percentage of air spaces, or voids in the mineral mixture, and vary with the character and shape of the particles of stone used in each particular case. After the proportions have been determined, the mineral material is passed through a rotary dryer, from which it is carried up an elevation and through a rotary screen which separates the mineral material into its different groups of sizes. The proper proportion by weights of each of these sizes is secured by a scale having seven beams, the exact required amount being weighed out, and run into a double shaft rotary mixer. Then it is combined with a bituminous cement which is also accurately weighed in the proper proportion. The whole is then thoroughly mixed together and dumped, while still hot, into carts, hauled to the street and spread as stated above and thoroughly rolled with a heavy steam roller.

After the surface is thoroughly rolled, a flush coat of quick drying bituminous cement is applied to the surface, thoroughly sealing it and absolutely preventing the penetra-

tion of moisture. There is then applied a thin layer of hot finely crushed stone, varying from $\frac{1}{4}$ to $\frac{3}{4}$ in. in size, according to the roughness of the surface desired. The pavement is then again thoroughly rolled leaving the street in a finished condition.

By using a coarse mineral grain (hard crushed stone), from 1 to $1\frac{1}{2}$ ins., down to an impalpable powder, the voids are reduced to about 10 per cent and by completely filling these voids with a bituminous cement that is absolutely unaffected by water, a thoroughly water-proof and air-proof wearing surface is made which precludes the disintegrating influences of air and moisture. The attack can come only from the surface, and under these conditions is so slow as to give the pavement a very long life. The coarse grain also affords a gritty surface which gives a good foothold for horses.

As the stone supports the traffic it is not necessary to rely upon the bituminous cement, to give the necessary rigidity to sustain traffic. The bituminous cement makes the pavement water-proof and binds the mineral ingredients together so as to prevent the action of water and the picking out of these particles by the horses' hoofs. The cement used is so soft that the pavement will not crack in cold weather and as the stone itself sustains the traffic the softness of the cement is no detriment in summer. After five years' experience in cold climates no bitulithic pavement has cracked in the slightest degree.*

*Correspondence with Warren Brothers Co., by S. F. P.

CHAPTER XIX.

THE OILED ROADS AND STREETS OF THE PACIFIC COAST.

These roads and streets are mainly the result of conditions prevailing in the southern counties of California. "Soon after the discovery of oil at Summerland on the southeastern coast of Santa Barbara county in 1894, oil was used in a small way in the immediate vicinity of the wells, the first application being made to the road surface of Ortega Hill, on the borders of Summerland. From that small beginning the use of oil on roads was extended until it is the favorite method of that section for laying dust and making a good all-the-year-round road. In some cases the roadbed has been plowed up, harrowed, and leveled, and then the oil worked in with a spiked roller. In other cases it is sprinkled on the road where dust prevails and allowed to settle into the dust until it packs from the passing of wheels. Where there is no dust and the road is quite hard, sand is sprinkled on after the oil is applied, to take up the surplus so that the surface will pack under the wheels. The best results have been secured by applying the oil when the surface of the road was covered with a sandy dust of not too great depth, about 1 in. being most satisfactory. In applying the oil there has been used a sprinkling cart with an apparatus regulating the flow of oil according as it is thick and heavy, or light and more fluid. Some of the country roads are oiled the width over which the sprinkler distributes the oil at one passage. When the travel is greater twice that width is sprinkled, making an oiled strip of perhaps 20 ft. in width. Sixty barrels will give a mile of road one application the width of the sprinkler, or from 100 to 120 barrels for double that width. The heavier the oil the more satisfactory the results from the same quantity. The interval allowed between the first and the second application of oil depends much upon local conditions, character of the roadbed, etc. The first application should be

thoroughly incorporated with the soil before the second is put on. Special attention should be given to where the soil is particularly loose, and larger quantities of oil applied at such points. Generally as much oil has been used on the second application as on the first, although after a second application under usual conditions the quantity may be reduced each time. It is seldom that more than a fourth application is necessary to produce good results. The oil is heated so that it will flow more readily from the sprinkler. It is no longer considered necessary to heat it so far as its effect upon the roadbed is concerned. The lighter the oil the less need for heating. It is generally heated by steam to 180° to 200° F. at Summerland, but by the time it reaches the points of application to the roads in the vicinity the temperature has dropped to 125°. As the oil that is not used in the neighborhood is usually heated to drive out the water found in connection therewith, there is little or no extra charge for supplying heated oil. The specific gravity of the Summerland oil is from 12° to 16° B. The expansion caused by heating depends upon the specific gravity of the oil and the quantity of water contained therein. It is said that a 10 per cent increase by expansion would probably be an average, although very much depends upon the quantity of water contained in the oil. The oil used in the vicinity of Santa Barbara is obtained at Summerland, 5 miles east of the city, and has varied in price from 40 to 60 cents per barrel of 42 gallons. The average cost per mile of applying to the road is about \$15.00, estimating a haul of from 5 to 10 miles. As to the amount and frequency of subsequent applications, everything depends on the character of the surface soil. Various kinds of soil abound—adobe, red clay, alluvial and sandy. If it be such that the oil forms by admixture with the sand a species of asphaltum pavement, an effect that has been noted in some instances, then the road is easily kept in order. If, however, the oil does not readily amalgamate with the soil, and the passage of vehicles tends to break up the surface into small particles, then the oil must be applied until a good wearing surface is obtained. The most troublesome natural disadvantage encountered in maintaining oiled roads in good condition has been the lack of homogeneity in the soil, some

being hard and some soft. The more nearly the road surface is made homogeneous the better are the results from the application of the oil."

"When the soil is very sandy, through the use of a large quantity of oil excellent results are produced. By using a fine gravel with the oil a better road is secured with less oil. Where there is so much loose sand, in some places it is almost impossible to get enough oil in it to keep it from breaking up under the passage of heavy teams and vehicles. It has been demonstrated that it is less expensive to make the road-bed solid by graveling than to build it of sand and oil. It requires only about one-fourth as much oil to make a good road when a gravel base is provided as it does to make a road entirely of sand and oil. The gravel base, if properly constructed, withstands the wear and waste by heavy traffic and, with additional applications of oil, as the volume of travel requires, develops a permanent surface, more substantial, and in less time, than in the case of roads built upon the natural sand alone."

"In the first stages of the experimenting with oil sprinkling, there were objections by some people to this method of improving the highways, because of the fact that when the oil was first applied it rendered the road disagreeable to travel on, and had a tendency to soil vehicles and clothing. This, however, proved to be of only temporary duration, as a few days, when the oil had been properly worked in and the surface smoothed and packed by thorough rolling, sufficed to harden the surface and keep it clean. It was soon realized that the inconvenience caused by the first application of oil was not nearly so great as was caused by the first application of gravel. In the latter case it requires nearly a year for the road to become packed and smooth, while with oil the time required to put the road in readiness for easy and dustless travel is only a few days. Oil has the advantage over water in the fact that where applied there is absolutely no dust, and when the roadbed is properly prepared there is practically no mud during the rainy season. In the matter of expense, as compared with watering roads to keep down dust, the use of oil has also a decided advantage."

"The White and the Glover road-oilers are used. On the whole, the roads so far have not been affected by storm waters. Summer heat has been detrimental in a few instances, and rows of shade trees are regarded as a benefit."

"The city of Los Angeles began oiling streets in 1901. The soil is generally gravelly, in some places black loam, in others sandy loam. The oiled streets vary from 30 to 60 ft. between curbs and in most cases are oiled the full width. The blocks vary from 400 to 600 ft. square. In preparing the street for oiling, the surface is brought to subgrade and covered with a layer of gravel 5 ins. thick, after thorough rolling while moistened, containing no stones larger than $2\frac{1}{2}$ ins. in diameter, and well rammed 1 ft. in width along gutters and curbs. On this is spread a top layer of gravel, 3 ins. thick after rolling and packing as before, containing no stones larger than 1 in. in diameter. The entire surface is then broken and stirred to a depth of 2 ins. by a fine-toothed harrow. Oil is then applied, usually at the rate of 1 to $1\frac{1}{2}$ gallons per sq. yd. At least 12 hours, usually 24, are allowed to elapse, when the surface is again harrowed and a second coat of oil put on, the quantity being proportioned so that the total amount used for the two applications shall not be less than two gallons per square yard of street surface. Places where an excess of oil occurs are sprinkled with sufficient sharp sand to absorb the same, and portions which appear too dry receive a further light application of oil. The oil used is crude petroleum from the Los Angeles wells, of specific gravity 11° to 14° B. and costs 65 cents per barrel at the tank. It is heated by steam to 180° F. for both applications. The cost of making the first application, in addition to the cost of the oil, is about \$200 per mile. Chuck-holes are the principal trouble dealt with in maintaining the oiled streets, which require some reoiling, according to condition each year."

"The experiences of forty counties, extending from Tehama on the north to San Diego on the south, a distance of 600 miles, cover the subject thoroughly. In the beginning, oil was used as a substitute for water to lay the dust of roads more cheaply. Its efficiency for this purpose was quickly recognized, and through the hardened and lasting surface obtained, road-makers were led to its use in making permanent

road surfacing. It is along this latter line that such remarkable success has been attained. Undoubtedly the work of the future will be the developing of oil surfacing to the point where can an artificially bitumen-covered roadbed will be had."

"Careful work should be had in the preparation of a road that is to be oiled. If an earth foundation is to be dealt with, it should be worked until a uniform density is obtained. In the case of macadam or graveled roads, they should be smooth and free from weak and wornout spots. No one would think of laying an asphalt pavement without first obtaining a firm and uniform foundation."

"In the application of the oil to any surface no pains should be spared to get an equal distribution, and a liberal sanding to hold the oil in place on the crowned surface. Again, the sand not only retains the oil in position, but is incorporated with and thus gives the real body to the contained asphaltum. The bearing power of the surface is greatly enhanced by the proper saturation of sand with the oil."

"The effort in securing a good foundation, properly graded and drained, and the careful application of oil and sand, will be amply repaid in a good road."*

The preceding pages, quoted from the Official Bulletin of the Department of Highways of the State of California, are not without value to roadmakers in other sections of the country. The insistence with which a good foundation, properly graded and drained, is demanded is to be especially noted and regarded. While it is not to be asserted that oiled roads cannot be successfully constructed in regions subject to frost, it is not likely that they can be constructed in the same manner as they are constructed in California where frosts sufficiently severe to disturb earth foundations are unknown.

Moreover, it must again be borne in mind, and never forgotten, that the petroleum oils of California are created of such a peculiar composition that when exposed to the atmosphere, by evaporation and chemical reactions, they are converted into asphaltum. It would, therefore, be expected that from natural causes a roadbed of sand, saturated with California petroleum, would become a roadbed covered with a

*Oiled Roads of California. Bulletin No. 2. October, 1904.

solid bituminous concrete, especially if the sand was mixed with gravel. It would therefore, again, be a fatal mistake to suppose that a roadbed saturated with any of the petroleums found in the Mississippi Valley, which never form asphaltum from natural causes, either by evaporation or chemical changes, would ever become covered with a sheet of solid bitumen, wherever it might be constructed.

The only attempt to construct such a road within my personal knowledge was made in the summer of 1906, on one of the state roads being constructed a few miles west of Wickford, R. I. The new roadbed has been sprinkled with crude petroleum. The result was inappreciable, except that the road had the odor of crude petroleum. A similar oiled road was observed between Pittsfield and Lenox, Mass., in August, 1908, and others in that neighborhood in 1909.

Petroleum has also been used in California to lay the dust on the road beds of railroads in place of ballast. Several applications are necessary. The oil serves an additional purpose of killing the weeds along the track. Both the great railroad systems of California, the Southern Pacific and the Santa Fe, have used oil with satisfactory results.

CHAPTER XX. ASPHALT BLOCKS.

Asphalt blocks consist of a aggregate of crushed stone cemented together with bitumen under great pressure in the form of large bricks. The molding is done in machines invented for the purpose, of which there are several that differ more or less in mechanical construction. The best machine is the one that with the least expenditure of power will make the most compact blocks of the most uniform size; both of which properties are essential elements of good blocks.

Experience has proved that a hard unweathered trap rock or limestone or cement rock, or a rock that will make neither good lime nor good cement, but is both hard and tough, and, like trap rock, is only slightly crystalline, is most suitable. Very much depends upon the crushing of the stone. It should be angular and not flaky. This consideration is one that gives trap rock its superiority over almost every other rock. The parallel bedding of the trap has been destroyed, and, unlike rocks that are not metamorphosed, its fracture is angular. It is very important that the sizes of crushed stone should be graded, from the largest size, to an impalpable dust, in such a manner that while about 70 per cent of it will pass a circular hole $\frac{1}{4}$ in. in diameter the different sizes should very closely approximate those in the following table. The sizes that will not pass a $\frac{1}{4}$ -in. hole should contain very few pieces half an inch in dimensions, and there should be none larger.

Table of Dimensions of Crushed Stone.

Sieves.	Percentage for test voids.
Passing 200 meshes to linear inch.....	11.4
Passing 100 meshes to linear inch, retained on 200.....	3.0
Passing 60 meshes to linear inch, retained on 100.....	5.5
Passing 40 meshes to linear inch, retained on 60.....	5.5
Passing 30 meshes to linear inch, retained on 40.....	5.2
Passing 20 meshes to linear inch, retained on 30.....	7.1
Passing 16 meshes to linear inch, retained on 20.....	4.1
Passing 10 meshes to linear inch, retained on 16.....	13.0
Passing $\frac{1}{2}$ meshes to linear inch, retained on 10.....	16.2
Passing $\frac{1}{4}$ meshes to linear inch, retained on $\frac{1}{8}$	29.0

Any deficiency in the smallest size can best be filled with a cheap quality of hydraulic cement or with powdered quicklime, either of which will correct any slight acidity in the asphaltic cement or residuum oil.

The proportions of asphaltic cement and stone are weighed out and thoroughly mixed in a mixer, where they are automatically passed to the molding machine in amounts just sufficient for a single block. The size of the blocks is 12x5x3 ins., with an allowed variation of $\frac{1}{4}$ in. This variation gives a maximum deviation on the line of jointing of $\frac{1}{2}$ inch, which is twice as much as it ought to be, as the writer has found a maximum variation in blocks made by the same machine to rarely or never exceed $\frac{1}{8}$ inch.

The proper laying of the blocks is edgewise, presenting a single surface of 12x3 ins. They are, however, often laid flat, presenting a single surface of 12x5 ins. Mistaken ideas of economy prompt this latter procedure, in which the danger of breakage under unusual strain is enormously increased. The blocks are properly laid on 6 ins. of Portland cement concrete, with a cushion of sand between the surface of the concrete and the blocks.

An unyielding foundation is an imperative necessity to insure a durable asphalt block street.

The best asphalt blocks have been made, so far as the writer is informed, of well refined Trinidad pitch, fluxed and thoroughly blended with residuum oil that contains little or no crystallizable paraffine. The bitumen, when removed from the mineral aggregate by solvents, should be soft, very viscous and adhesive at ordinary temperatures. It should not be brittle at any temperature to which the street is likely to be subjected under traffic. No hard and fast rules can govern such requirements, as they vary and should be determined for each locality. It should always be borne in mind that the bitumen holds the stone together and that the stone, not the bitumen, receives the wear of traffic. The bituminous aggregate, therefore, should be soft, tenacious and adhesive, rather than hard, tending to brittleness, and while sufficient in amount should not be excessive. It is a mistake to suppose that a poor quality of bitumen can be compensated by increasing the amount. Good blocks cannot be made with

either stone or bitumen deficient in the required qualities. An excess of such bitumen aggravates the evil.

Good asphalt blocks, properly laid, make a clean, durable and very satisfactory street.

CHAPTER XXI. WOOD BLOCKS.

Wood blocks are prepared for pavement by sawing rectangular blocks, from sound heart wood timber, $3\frac{1}{2}$ in. (parallel with the fiber), by 3—4 ins. by 6—10 ins. All of the blocks used on a single contract must be of the same kind of timber and of the same width.

These blocks are treated in a vacuum apparatus with an antiseptic and waterproof mixture consisting of heavy oil of coal-tar mixed with rosin. The proportions vary. The mixture should be very fluid when hot and wholly free from solid matter that would gather upon the exterior surface of the blocks and prevent the complete saturation and impregnation of the blocks with the fluid mixture.

The blocks are placed in an air-tight cylinder in which heat is raised and maintained at 215° F. for a sufficient length of time to insure the heating of the entire mass. The time will depend upon the size of the cylinder. The heat is then raised to 285° F. and maintained at that temperature until the blocks are completely sterilized. Application of heat is then stopped and the temperature of the cylinders allowed to fall until it has been reduced to 250° . A vacuum pump is then applied until the entire mass within the cylinder is completely deprived of both water and air, or until the vacuum is at least 26 in. When it is absolutely certain that every block in the cylinder is free from water and air under as complete exhaustion as the apparatus is capable of producing, not less than 26 ins., the bituminous mixture is run into the cylinder at a temperature of 175° to 260° F., after which hydraulic pressure, of not less than 200 lbs. per sq. in., is raised and maintained until every block is completely saturated with the mixture.

There are several important factors to be regarded in the successful use of this process for this purpose.

First, the vacuum pumps must be of a size somewhat in excess of the theoretical maximum required.

Second, not a single step in the process can be successfully performed in haste. No matter what the size of the pumps may be in proportion to the size of the cylinder, the successful heating of the mass of blocks in a large cylinder, and of the complete removal of the vapor of water and air under a continued vacuum of 26 ins., requires time, and I have no doubt that it will be found in practice that there is a limit to the profitable operation of large apparatus.

Third, complete saturation of all the blocks that go into a street, no matter what kind of wood may be used, is the critical consideration in the preparation of wood paving blocks. Any kind of wood completely saturated is to be preferred to the most desirable wood only partially treated. I have examined blocks made of every kind of wood used in New York City and treated with every kind of oil used for that purpose. I have found among the different samples, blocks only smeared outside with oil and completely wet with water inside; also, blocks fully saturated with light oil, and also with the heaviest oil used. It is absolutely impossible to drive oil by any amount of pressure into the pores of wood filled solid full with water. The water and air must first be driven out before the oil mixture can be driven in. The time required for heating and exhausting must be determined for each apparatus separately, and it should be done with the greatest care.

Fourth, the wear of traffic is borne by the wood and not by the bitumen with which it is saturated. The bitumen preserves the wood from decay. If on an average one-third of the blocks are filled with water instead of bitumen, it need occasion no surprise if street surfaces where such blocks are laid soon become conspicuous failures, from the presence of decayed blocks.

Fifth, all timber should be seasoned under cover and then kiln dried, to avoid checks and also to reduce the time to its lowest terms required to pump out the vapor of water. Checked blocks should be avoided, because the checks make the blocks weaker, and also because it is quite difficult to fill the checks completely, with the oil mixture.

A good wood block street is very good indeed, but when it is bad it is horrid.

CHAPTER XXII. CONCLUSIONS.

A careful perusal of the foregoing pages leads to several conclusions that express fundamental truths. They may be briefly stated as follows:

First, that all bituminous streets and roads require as a fundamental prerequisite a solid, unyielding foundation, either of rolled and tamped soil, that has no soft spots, or, 6 ins. of concrete, made of the best Portland cement mortar, 1 part cement to 3 parts of clean, sharp sand, the mortar to be mixed with 5 parts of clean, unweathered broken stone. No more false economy can be indulged than to make a foundation of natural cement mortar, soft, weak, and porous; or, to use soft, weak, weathered stone that has not the strength of the cement mortar. Nor should repairs be allowed so carelessly made as to replace concrete with that which is weaker than that originally put down. Such grave mistakes are prolific sources of dissatisfaction with bituminous streets, in which city officials and citizens share an equal loss, both in money and temper.

Second, the source from which the bitumen is obtained is of little concern, provided it be suitable; that is to say, it shall be either protected from water or not acted on by water.

Third, the concrete should be swept clean and as dry as possible, with preferably a rough surface. Before laying the bituminous surface, whether it be wood block, asphalt block, bitulithic or "sheet asphalt"—it is not enough that the concrete be swept clean, but it should be dry as well as clean. The water in or on a wet, cold concrete, whether frozen or not, cannot escape after the bitumen is put down. It remains to prevent the adhesion of the concrete surface with bitumen. If they do not adhere, the water expands under the heat of summer and assists the movement of the sheet of bituminous surface mixture from the center of the street to the curb. If a binder is used it becomes embedded in the surface mixture.

and moves with it. A moving surface rolls, wrinkles and blisters, finally breaking beneath traffic, cracking in extreme cold and breaking down to the concrete. It is a fatal mistake to lay bituminous surfaces of any kind in wet, cold or frosty weather or before the surface of the concrete has thoroughly dried out. Hot, clear weather is the time in which to do such work.

Fourth, a binder course an inch in thickness which evens up the inequalities of the cement, that is made of stone of nearly uniform size, from which the fine particles have been screened, and consequently is full of holes, is of very doubtful value as a part of a bituminous street. If laid at all, it should be laid on a solid concrete impervious to water from any source. It should be free from voids, by grading the sizes of stone precisely as they are graded for asphalt blocks, using the bitumen, not to coat, or smear the, surfaces of comparatively large pieces of stone with large spaces of void between them, but to completely fill the small percentages of voids that remain between the fragments of stone graded for "least voids." Such a binder might be laid on dry concrete with a very soft bitumen that is not affected by water and thus form a solid protection to an immovable asphalt street mixture, that like bitulithic would only be attacked by the atmosphere from the surface.

In the judgment of the writer, an unfortunate lack of technical skill and appreciation has been exhibited in the construction of binders. All sorts of mineral and bituminous rubbish have been found in some of them. They have been laid with such a large proportion of voids that traffic has soon forced the surface into the binder until the whole mass was but little more than 2 ins. thick and had every appearance that the bitumen of the binder had been absorbed by the surface, leaving the dry binder stones almost loose and with little or no adhesion to the concrete. Such a binder is no binder at all, and in the judgment of the writer, is worse than nothing.

Fifth, the mineral aggregate of the wearing surface should be a hard, sharp sand that should all pass a No. 10 screen and should be graded in such sizes as will insure least voids. If the sand is deficient in fine dust passing a 200-mesh

sieve, the proper amount should be added in a good quality of natural cement, though Portland cement would be better. The term "inorganic dust," under which all sorts of soil, clay, weathered screenings and inorganic rubbish, that will absorb water, have been specified, has no place as designating an ingredient of a wearing surface.

The bitumen should be selected with reference to the climate of the locality where the street is to be put down. So much depends upon what is put under a street surface that no hard and fast rules can be laid down to govern such selection. The opinion has been generally advanced that Franklin avenue, Buffalo, N. Y., owed its lasting qualities to wax tailings, but streets have been laid of Trinidad pitch that were not fluxed with wax tailings, that were both very satisfactory and very unsatisfactory. It, however, must be admitted on Mr. Abbott's description that the surface mixture on Franklin avenue was underlaid with a waterproof binder, that it is highly probable had as much, if not more, to do with the permanance of the street than the wax tailings. If I had the 3 ins. of waterproof bituminous concrete on an immovable base that was laid on Franklin avenue, I would not hesitate to put on it any surface that had proved elsewhere to make a good street. There is no question that a residuum oil that is as free as possible from solid paraffine and paraffine oils is suitable for use as a flux about in proportion as its properties approach those of wax tailings. Nevertheless, a good asphalt street results from the concurrence of a number of requisite conditions, and the absence of any one of them may cause disaster, when all the others are present.

The conclusions herein expressed have been reached with regard to only one result, and that is a good street, with the conviction that the cheapest is not always the most economical, nor is the lowest bidder always to be preferred.

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